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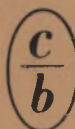
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Publication therefore did not occur prior to this date, but must be assumed
to have taken place reasonably soon thereafter.*

The paper examines principal concepts of the sources of metals accumulated in hot springs and hydrothermal-sedimentary ore shows in the rift zones of the world ocean. A critical analysis is made of the experimental studies on interaction of basalt from spreading zones with seawater. The importance is shown of the magmatogenic source in supply of sulfide-forming elements.

The sources of ore-forming metals are a crucial and, at the same time, most debated issue in the theory of hydrothermal-sedimentary metallogeny (Fe, Mn, Zn, Cu, Pb, etc.). Identifying the sources is essential, not only for theory but also for practice, because they largely predetermine the geochemical features, locations, and economic value of deposits of various genesis.

Recent hydrothermal and hydrothermal-sedimentary metalliferous formations of tectonically active regions of the oceanic crust are a valuable object for studies of metallogenic processes, because their mineralogic and geochemical traits remained almost unaffected by secondary alterations and represent the composition and properties of thermal solutions and the physical and chemical conditions of the sedimentation environment. Before discussing the existing notions of the sources of the elements taking part in these formations, we will describe the features of their mineral and chemical composition, and consider some information on the contents of ore elements in Recent thermal solutions.

The geochemical specifics of ore in the oceanic crust are manifest in sulfide mineralization, which concentrates the bulk of metals brought by hot springs; the influence of exogenous and, especially, sorption processes, on the chemistry of deposits is minimized; and the contribution of biogenic and terrigenous sedimentation is also minimal.

Hydrothermal sedimentary sulfide formations (massive bodies on the seafloor in open ocean, and bed-shaped lenses in the depressions of the Red Sea) exhibit a variety of mineral species, with predominance of iron, copper, and zinc sulfides.

Sulfide minerals - pyrite, chalcopyrite, sphalerite, wurtzite, pyrrhotite, and chalcopyrrhotite - are widespread; also found in minor amounts are marcasite, bornite, vallerite, degenite, chalcosite, covellite, and compound copper sulfate salts; lead sulfides (galena and jordanite) have only been found in trace amounts at 21° N lat. in EPR [28, 36, 41, 45].

The numerous chemical analysis of sulfide deposits from various locations in the rift zones (Table 1) reveal a relatively clear picture of their geochemistry.

The data given in Table 1 show that all hydrothermal sedimentary sulfide formations of the ocean floor currently known have high contents of Fe (up to 45%), Zn (up to 45%, in single cases up to 60%), and Cu (up to 6%, in some sites up to 30%). While their proportions vary, the sum total of these elements usually is larger than 50%; the sulfides of these metals make up the bulk of ore accumulations. The typical accessory elements are the following, ppm: Pb up to 6000, Cd up to 1000, Ag up to 480, As up to 1000, and Au up to 10.

Characteristic features of seafloor sulfide geochemistry are low contents of Ni and Cr (from units to tens of ppm) and usually low Co concentrations, which rise to one hundredth of a percentage point in single specimens.

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 3-18, November-December, 1986. Original article submitted April 14, 1986.

TABLE 1. Element Contents in Sulfide Sediments of the Rift Zones*

Object of studies	Specimen No.	Fe	Zn	Cu	Pb	Cd	Ag
21° N lat., EPR [28, 30]	1	14,7	34,9	0,23	0,61	120	241
	2	26,2	20,3	1,3	0,07	890	34
	3	16,7	41,8	0,89	0,29	790	202
Juan de Fuca Ridge [28,41]	1	2,19	61,0	0,08	0,20	1060	230
	2	41,4	2,27	0,04	0,27	8	15
	3	15,6	46,9	0,35	0,30	490	290
13° N lat., EPR [37]	1	30,6	0,04	31,6	0,002	4	Not found
	2	15,0	0,25	2,6	0,003	12	6
	3	26,4	14,0	2,9	0,09	815	79
	4	14,7	41,7	0,32	0,24	557	186
Galapagos rift zone [26, 28, 43]	1	44,1	0,14	4,98	0,07	32	10
	2	38,0	1,0	6,5	0,02	Not det'd	21
	3	1-45	0,05-50	0,3-11	0-0,1	0-700	0-480
Red Sea (Atlantis-II Deep)	1	34,1	17,4	0,42	0,11	Not det'd	Not det'd
	2	12,6	15,0	0,9	0,21	150	60
	3	25,9	1,58	1,3	0,03	Not det'd	20
Cyprus Ophiolites [32]	1	32,1	11,8	5,3	0,22	500	75
Basalts from spreading zones of the ocean [31, 40, 54]	1	6,5	0,0078	0,0081	0,0002	0,128	0,03

*Fe, Zn, Cu, Pb contents in %, other elements in 10⁻⁴%.

Magmatic sulfides dispersed through the groundmass of basalt have an entirely different composition. Widespread are sulfides of Ni, Cu, and Fe (pentlandite, chalcopyrite, pyrrhotite, pyrite, and complex high-Ni and -Cu sulfide compounds). The high nickel content in the primary magnetic sulfide and the almost complete absence of lead and zinc are the characteristics of these formations noted by many investigators [15, 36, etc.]. Ni/Cu ratio, both in sulfides and in the silicate matrix of basalts, declines from the primitive varieties to more differentiated modifications, showing that nickel, more than other elements, enters the crystalline phases in early stages of basalt crystallization. The high-nickel sulfide deposits are also known to be associated genetically with deep magmatic intrusions.

In addition to primary magmatic sulfides, the basalts of oceanic crust include disseminated minerals and insets and veins of secondary mineralization, mainly Fe and Cu sulfides, with virtually no Pb, Zn, and Cd - elements characteristic for seafloor ore accumulations, and Ni - a typical elements of magmatic sulfides [2, 13, 16, 20, 29, 48].

The geochemistry of Recent hydrothermal-sedimentary sulfide formations is largely observed also in ancient pyrite deposits, many of which, according to current theories, belong to the same genetic type. Some authors believe them to be a product of submarine discharge of hot springs. Although the mineral compositions may vary, the main components are Fe, Cu, Zn, and Pb sulfides, with Cu contents typically decreasing with in a deposit from top to bottom and laterally, with increasing distance from the hot springs. The vein mineralization, as in the Recent process, is usually associated with a higher content of Cu and Fe sulfides.

Among nonsulfidic phases common in metalliferous sediments are oxides and hydroxides of iron and manganese (x-ray amorphous, goethite, lepidocrocite, hematite, magnetite, manganite, todorokite, and other minerals).

The hydrothermal (endogenous) component of metalliferous seafloor deposits thus is composed of the following metals: Fe, Mn, Cu, and Zn; the typical impurity elements are Pb, Ag, Cd, As, and Au; other metals, such as Co, Ni, Cr, and Ti, are contained in amounts which are usually by one, two, or three orders of magnitude lower than their mean concentrations in basalts.

The data on the chemical composition of hot springs in the rift zones of world oceans collected in the past few years are in full agreement with the geochemical features of hydrothermal-sedimentary ore shows. The data of Table 2 confirm that the hot springs are enriched in elements of the same group as those accumulated in metalliferous sediments (Mn, Fe, Cu, Pb, Ag, Cd), as compared with seawater. Some specimens exhibited heightened Co contents, while Ni contents in all specimens were below the sensitivity of the measurement method [52, 53].

Au	As	Hg	Sb	Sn	Co	Ni	Cr
Not det'd	483	2	45,0	1	2	2	8
0,17	770	1	13	1	2,5	5	16
0,2	245	1	52,9	1	6	2	30
0,1	235	5	Not det'd	1	6,4	8	8
0,1	430	1	"	1	1,2	8	12
0,13	411	1	"	1	24	Not det'd	8
Not det'd	Not found	Not det'd	"	Not det'd	160	40	Not det'd
"	45	"	"	"	500	10	"
"	1253	"	"	"	30	50	"
"	184	"	"	"	50	90	"
0,05	125	"	"	1	482	3,1	55
0,2	45	"	"	Not det'd	250	Not det'd	Not det'd
Not det'd	Not found	"	"	0-300	0-500	"	"
"	"	"	"	Not det'd	132	18	"
"	"	"	"	"	Not det'd	Not det'd	"
"	"	"	"	"	"	30	"
"	"	"	"	"	"	Not det'd	"
0.0012	2,0	0,69	1	1,5	65	144	317

The variations of the chemical composition of hydrothermal solutions are mainly correlated with the environments of their discharge. At 21°N lat. hot springs exit from cracks in oceanic basalts, forming "black smokers" - ore material is deposited as the hot springs mix with normal seawater, and metalliferous solutions are cooled and neutralized. The composition at the sites of discharge is controlled by temperature and acid-alkaline properties, which depend on the flow rate of the source; the latter in turn affects the degree of mixing of hot springs and seawater.

The relationship between metal concentrations and the temperature of the solutions is clearly seen in hot springs at 21°N lat. of EPR. The temperature of hydrothermal solutions in specimens 1 and 2 with the highest elements contents, according to [53], is 350-355°C, pH 3.3-3.4, while in specimens 3 and 4 the temperature drops to 270-275°C, and pH rises to 3.6-3.8. In these samples, the concentrations of all sulfide-forming metals are much lower, probably due to partial precipitation of sulfides along the routes of migration of the solutions, where the first to be extracted from the solution are elements such as Cu and Ag. In [45] it was demonstrated that Cu sulfides with heightened Ag content are common in the walls of metalliferous channels, especially minerals such as tennantite (Cu, Ag)₁₀(Fe, Zn, Cu)₂As₄S₁₃. Insets and veins of mineralization within basalts are also associated with widespread copper sulfides, as mentioned earlier.

The sequence of precipitation of metals, which determines the vertical and lateral mineralogic and geochemical zonality, largely depends on the stability of the complex compounds, which serve as vehicles for metal transport. This problem has been studied in [5] with special reference to metalliferous deposits of the Red Sea.

In Guaymas basin (the Gulf of California), the metalliferous solutions migrate through thick biogenic-terrigenous deposits, and emerge to the surface "processed" to different degrees, i.e., after depositing a large portion of their metal load along the paths of migration through the sediment. The temperature at the exit varies from 315 to 25°C [52]. Although the solutions in the Gulf of California are depleted of the ore-forming metals, the spectrum of the elements coincides fully with the chemical features of the hydrothermal solutions discharged on the seafloor in open ocean, leading to the hypothesis that the primary composition in the two regions was the same [52].

Representative data on the composition of thermal solutions and the ore accumulations on the seafloor formed by discharge of these solutions thus provide a reliable judgment about their geochemistry and the set of endogenous ore-forming (and accessory) chemical elements.

Most studies discussing the genesis of hydrothermal-sedimentary formations of the oceanic crust, and in particular the sources of the ore material, regrettably, do not examine the specific factors controlling the features of the chemical composition of ore deposits. In

TABLE 2. Concentration of Metals in Thermal Solutions of Rift Zones*

Object of study	Speci- men number	Mn	Fe	Cu	Zn	Ag	Cd	Pb	Co	pH
21° N, lat., EPR [53]	1	52,7	92,93	2,3	6,9	4,1	17,4	63,8	12,5	3,4
	2	48,2	135,6	2,8	6,8	4,0	20,2	74,4	13,3	3,3
	3	38,4	41,9	0,6	5,8	2,8	16,2	40,2	3,9	3,6
	4	55,05	48,65	0,001	2,6	0,1	1,9	37,9	1,3	3,8
Gulf of California, Guayamas basin [52]	1	7,6	3,1	< 0,001	0,3	24,8	< 1	54,9	< 0,3	5,9
	2	12,2	2,7	< 0,001	0,1	< 0,1	< 1	63,0	< 0,3	5,9
	3	12,9	10,0	< 0,001	2,6	2,6	< 1	135,1	< 0,3	5,9
	4	7,6	4,3	0,06	1,2	0,2	5,2	47,6	< 0,3	5,9
	5	7,0	1,8	0,006	0,14	< 0,1	3,0	< 4	< 0,3	5,9
	6	8,1	0,95	< 0,001	0,06	< 0,1	< 1	< 4	< 0,3	5,9
	7	7,6	2,1	< 0,001	0,14	< 0,1	< 1	< 4	< 0,3	5,9
	8	7,2	4,6	< 0,001	1,4	< 0,1	< 1	< 4	< 0,3	5,9
Red Sea [4]	1	90	94	0,23	7,84	Not det'd	Not det'd	230	7,8	∞3,5
	2	86	87	0,33	9,2	»	»	320	4	∞3,5
	3	87	90	0,14	5,36	»	»	190	3	∞3,5
Seawater [33, 42]		$2 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$1-3 \cdot 10^{-3}$	$5-20 \cdot 10^{-3}$	$1-3 \cdot 10^{-4}$	$3-7 \cdot 10^{-5}$	$3-8 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	7,8

*Mn, Fe, Cu, and Zn contents in milligrams per kilogram; Pb, Cd, Ag, and Co contents in micrograms per kilogram.

other words, they do not trace the geochemical connections between the process of metallization and its ultimate form.

On the other hand, a hypothesis about the sources of ore material must take into account the actual distribution of elements in hydrothermal and hydrothermal-sedimentary metalliferous formations, and try to elucidate their geochemical characteristics. We will examine the prevalent theories in this field from that point of view.

A review of the large number of publications on sources of ore components accumulated in metalliferous and ore-bearing sediments of tectonically active regions of the earth, and particularly their rift zones, reveals two principal trends.

One group of another develop conventional views of ore exploration geologists, assuming the principal role of magmatogenic processes in the transport of metals by the fluid phase and formation of hydrothermal and hydrothermal-sedimentary ore accumulations, including sea-floor metalliferous sediments.

An alternative to the theory of magmatogenic origin of the ore is the hypothesis of the role of interaction of thermal solutions with oceanic crust rocks, which mobilized and supplied metals into the hot springs; this view is popular among some Soviet and many American geologists. The hypothesis of basalt lixiviation has become especially popular recently with the development of oceanographic studies, and in particular, deep-sea drilling. These studies discovered in the oceanic crust thick hydrothermal circulation systems, and offered an opportunity for direct analysis of hydrothermally altered rocks. This work stimulated a series of in vitro experiments, which in turn produced important results substantiating the hypothesis of hydrothermal lixiviation of basalts, and determining the principal contribution of this process to the development of a broad gamut of metalliferous sediments.

Laboratory experiments on the interaction of seawater with oceanic basalts in a broad range of P-T conditions and various proportions of seawater-rock components showed that seawater can leach out of oceanic crust rocks various chemical elements, including metals, demonstrating that in principle metalliferous solutions can be formed in this fashion.

In order to estimate the real value of this experimental work in demonstrating the crustal (basaltic) source of metals, we will review some of the results and compare the conclusions of different investigators.

A study of the interaction of basalts of midoceanic ridges with seawater by Seyfried and Motte [5] established that this process extracts from the silicate component of basalts almost all of Cu and Zn, the bulk of Ba, Sr, and Mn, and probably Co; V, Cr, and Ni remain unaffected by this process. A comparison of data on contents of trace elements in fresh and hydrothermally altered basaltic glasses, however, showed that Ni concentration in fresh glass was 146 ppm, as against 116-63 ppm in altered glass. The behavior of Ni during hydrothermal lixiviation of basalts thus remained unexplained, and the conclusion about its immobility was not confirmed.

Discussing the behavior of copper, the authors note that this element passes into solution only when parts of the experimental equipment are made of gold; it is assumed that Cu is extracted together with Au, i.e., that the instances of copper enrichment of the seawater reacting with basalts are artifacts [50].

Entirely different findings were obtained in experiments reported in [27, 49].

In [27] it was shown that at a temperature of 220°C and a pressure of 500 bar in a water-rock system with a ratio of 10:1, seawater extracts from basalts, along with Fe and Mn, only metals such as Ni and Cu; concentration of these metals in the solution is raised by 2-3 orders of magnitude, compared with normal seawater, while Zn, Pb, and Al remain practically immobile.

Subsequent experiments under similar conditions (T 300°C, P 500 bar, water-rock ratio 10:1) did not confirm these conclusions. In [49] the concentrations of the elements (Fe, Mn, Al, Ni, Cu) in the solution were given as observed after interaction with basalt. These data showed that only Fe and Mn passed into the solution, while Ni and Cu in all samples, regardless of the length of interaction (from 24 to 2208 h) were constant ($0.01 \times 10^{-4}\%$), and equal to their contents in the initial solution. The substantial increase of Fe concentration was at variance with data reported in the same article, which compared the iron contents of fresh

and hydrothermally altered basalts (Fe_2O_3^* concentration in fresh basalt was 13.29%, in altered basalt - 13.35%).

The numerous instances of contradictory and ambiguous conclusions based on experimental work clearly show that laboratory experiments at the moment do not describe adequately the behavior of metals in hydrothermal lixiviation of basalts, and do not elucidate the geochemistry or magnitude of supply of material by oceanic crusts; these studies shed little light on the problem of the source of metals.

Besides laboratory experiments, the proponents of the lixiviation hypothesis on the data on metamorphic alteration of the rocks of oceanic crusts based on dredging and deep-sea drilling. Unfortunately, while the mineralogic aspect of the process has been studied extensively, geochemical information in most instances did not determine any distinct patterns of behavior of elements during water-rock interaction. This process is so complex, that an element may be actively extracted from the rock in certain conditions and yet fall out of the solution in other conditions, forming secondary mineralization in basalts.

Petrologic and geochemical studies of hydrothermally altered oceanic basalt and ore-bearing rocks in pyrite deposits of the geologic past have revealed no clear traces of migration of ore-forming elements from magmatic rocks related spatially with hydrothermal-sedimentary ores [17, 20].

We see that neither in situ observations nor in vitro experiments of basalt lixiviation have produced a definitive answer as to the proportion and geochemical specifics of the crustal hydrothermally lixiviated component in the overall balance of metals accumulated in hydrothermal-sedimentary formations of the ocean floor.

It should come as no surprise therefore that investigators ascribe to basalt diametrically opposite roles as a source of the ore-forming components. This can be illustrated by the divergent conclusions of two studies derived from detailed petrochemical investigations of hydrothermally altered basalt (mainly based on deep-sea drilling) and balance calculations.

One study concludes that basalt is the main supplier of the ore component of hydrothermal solutions discharged on the ocean floor and beneath [8]; in contrast, in [21] it is stated that geochemical alterations of basalts during halmyrolysis and hydrothermal lixiviation cannot be the source of material for accumulation of metalliferous sediments and Fe-Mn nodules on ocean floor.

Besides the absence of rigorous geological, petrological, geochemical, and experimental proofs of a determinant role of lixiviation in forming the metallogeny of ore-forming solutions an additional argument makes this hypothesis even more vulnerable. The concept of basalt lixiviation is incapable of explaining the specific geochemistry of thermal solutions and ore accumulations on the ocean floor.

The reason for the extremely low concentration of Ni in these formations, for example, remains unclear despite its higher contents in basalts compared with Zn, Cu, and Pb (see Table 1). Since in basalts Ni is associated not only with hard-soluble sulfides, but with an easily decaying olivine, where NiO content varies from 0.19 to 0.50%, it is hard to see why there is so little of this element, not only in sulfide deposits on the seafloor, but in hydrothermal veinlets and secondary sulfide inlets in oceanic basalts.

In all hydrothermal-sedimentary sulfide formations of the rift zones, Cd is a characteristic and ubiquitous accessory element.

In oceanic basalts Cd occurs usually in very low, often trace, concentrations (its mean content in basalts from spreading zones is 0.128 ppm); the element has not been determined in any of the solutions obtained in vitro.

Generally there is a complete absence of a correlation between metal contents in the basalts of spreading zones and in the sulfide formations of the ocean floor (see Table 1).

The data on the composition of thermal solutions and on the geochemistry of hydrothermal-sedimentary ore mineralizations on the floor of the world ocean, and the results of laboratory experiments, give no sufficient grounds at least for now, for interpreting oceanic basalts as the only or even the main source of all ore-forming elements, including heavy

*Total Fe expressed in terms of Fe_2O_3 .

metals. Although some participation of the crustal source in hydrothermal-sedimentary metallogeny cannot be denied, the scope of its contribution to this process and the specific geochemistry are highly debatable.

Many investigators lean toward the notion of a magmatogenic supply into ore-forming hydrothermal system; in discussing the source of ore elements it is important to evaluate the geochemical contribution of this source.

In the last century, geologists realized the importance of volatile components in the segregation of chemical elements from magmatic melt. This idea was developed in classical works by F. M. Levinson-Lessing, V. M. Goldschmidt, A. G. Betekhtin, and A. N. Zavaritskii. Important contributions to the theory of degassing of the earth and the separation of the fluid phase from the magma were made by V. I. Vernadskii, A. P. Vinogradov, P. N. Kropotkin, D. S. Korzhinskii, P. Niggli, K. Krauskopf, and others. In recent years the theory of gas-water fluids as the natural components of magma-forming processes and the physical-chemical and thermodynamic aspects of this theory were developed successfully by A. A. Marakushev, I. D. Ryabchikov, V. S. Sobolev, L. N. Ovchinnikov, F. P. Letnikov, A. A. Kadik, and others.

Most recent submarine hydrothermal-sedimentary metalliferous and ore-forming entities are confined to areas of tectonomagmatic activity, and especially to rift zones. These zones are characterized by the maximum values of the thermal flow and features of intense degassing of mantle, as evidenced by numerous data on the composition, quantities, and isotopic characteristics of the gas phase of high-temperature hydrothermal solutions [6].

Within rift zones, a complex system of circulation of thermal solutions is at work; it consists of separate convection cells, where seawater penetrates to large depths (2-5 km) into the oceanic crust, is heated, metamorphosed, enriched in metalliferous components, and in the discharge areas produces a wide spectrum of metalliferous deposits on the seafloor and some ore mineralization in the subsurface zone of the oceanic crust.

Hydrothermal systems and ores associated with them are distributed along the rift zones locally and unevenly; the ore formation process develops in a pulsating pattern clearly seen both in Recent times and in hydrothermal-sedimentary deposits of the past [19].

In a large number of studies it has been shown that the magmatic regime of midoceanic ridges is also pulsational.

Since the energy substrate of the hydrothermal process is the plutonic depth, it is important to estimate the heat power of the discharge sources, and to determine the principal heat carriers.

Classifications of the vast volumes of data on the thermal balance of hydrothermal systems and calculations for Red Sea hydrothermal field, carried out by V. I. Kononov, led him to the conclusion that "... the heating of the systems cannot be supported solely by the off-take of conductive regional heat flow" and that "an additional influx of plutonic heat is required, which would be associated either with conductive heating from magma sources occurring at a shallow depth or with the influx of hot vapor-gas fluids" [7, p. 35].

All the above facts (the discrete distribution of hydrothermal cells, the pulsational ore-forming process in the magmatic regime, the presence of local heat and mass flows supporting the thermal energy of the geothermal systems, and the gas composition of thermal solutions) indicate the existence of a spatial and temporal correlation between Recent hydrothermal-sedimentary ore formation and intracrustal basaltic magmatism.

In the past few years the existence of such a correlation has been confirmed by data on localization of magmatic sources determined by geophysical exploration in various oceanic rifts at different, but mostly shallow, depths.

Detailed geologic-geophysical studies of the geothermal fields in the East Pacific Rise have determined magmatic chambers some 5 km wide and 3-5 km thick at depths of 2-3 km beneath the seafloor; a spatial correlation of hydrothermal activity and these magmatic chambers was determined [35]. Intermediate magmatic sources have been discovered also in the rift zone of the Red Sea [1] and in Iceland's geothermal fields [24].

Some authors believe that the main structures controlling the localization of high temperature hydrothermal systems are deep faults, or more specifically, the intersections of these faults with large zones of tectonic disruptions, which give rise to intermediate magmatic chambers associated with zones of pierced crust; through these zones mantle melts in-

trude periodically, and a flow of volatiles is released, which determine the gas regime of thermal solutions. Ample data on the correlations between hydrothermal cells in the oceanic crust regions and the specific tectonic structures in their evolution have been given in monograph [46].

The association between hydrothermal activity and intracrústal magmatic sources caused by local melting of the mantle seems to lead to the question of their possible role in the formation of the composition and the geochemical features of both the thermal solutions and the hydrothermal-sedimentary ore deposits formed as these solutions are discharged in the rift zones of the world ocean.

The concept of magmatogenic sources of the ore elements usually assumes that water-chloride fluids are separated from magmatic melts as they crystallize and cool, and that metals are carried with these fluids. Studies of the behavior and distribution of elements in the melts and supercritical fluids involve laboratory experiments which have been analyzed and generalized by S. D. Malinin and N. I. Khitarov [9]. These authors emphasized the role of chlorine and chloride complexes in the transition of ore components into the fluid, and their migration. Chlorine, which binds with metals to form unequally stable compounds, is a powerful agent for extracting elements from the melt. Experiments determined that for Zn, Cu, and Pb the distribution coefficients between the melt and the fluid are practically independent of the metal content in the melt, at least within an order of magnitude [22].

In [9] it was shown that the distribution of elements between the phases depends on the free energies of formation of their oxides: the higher these values, the lower the distribution coefficients (with other conditions being equal). In other words, the strength of retention of the metals in the melt is generally determined by the strength of their bonds with oxygen, i.e., the free energy of metal oxide formation, or their affinity to oxygen. It is assumed that the main form in which the metals (Zn, Cu, and Pb) exist in the melt is Me^{2+} , while in the fluid these are hydroxychloride complexes, such as $Me(OH)Cl$ [9].

The transport of metals in high temperature conditions by chloride complexes is confirmed by experiments and thermodynamic calculations [14, 38, 39]. Numerous finds of chlorides and hydrooxychlorides of metals amid products of Recent volcanic fumaroles also support this view. In high temperature sublimates, chlorides are also the principal carrier minerals of ore elements.

All this shows the importance of volatiles, especially chlorine, in extracting from the magma and transporting the ore material.

Under high pressures, chlorides of heavy metals usually have high volatility temperatures, while chlorine is well-solvable in the melt; chloride can therefore be separated from the magma at relatively small depth, which is indeed observed, as has been mentioned, in magmatic foci of the rift zones.

The motion of gas-water fluids is primarily controlled by a drop in the outer pressure when systems of cracks are created in overlying rocks.

One of the more complex and less developed aspects of the process of metallization is the chemical composition and properties of post-magmatic fluids.

An invaluable contribution has been made in this field by detailed and comprehensive studies of the greater fractured Tolbachik eruption (GFTE) (1975-1976), a study conducted by a large team of investigators [3].

The validity of applying the data about subaerial volcanism to the geochemistry of magmatogenic solutions, as part of determining the sources of material in oceanic ore formations, is based on the specifics of this particular eruption, in which assimilation of crustal material was virtually ruled out, as has been proved convincingly by detailed studies of the petrology of various types of GFTE basalts [18].

Unique data on the composition of gases released by degassing of basaltic melt and gas condensate from slightly degassed magma are of special value for understanding the sources of ore components; these releases can be interpreted as magmatogenic (mantle) solutions, unaltered by interaction with surrounding rocks, and representing the main characteristics of the primary material, temperature, and acidity of gas-water magmatic fluids.

These are ultra-acid (pH 0.25-1.76), overheated (930-1020°C), chloride-sodium-potassium water with extremely high contents of various trace elements. A comparison of the concentra-

TABLE 3. Extraction of Elements in Exhalation from Greater Fissured Tolbachik Eruption [11]

Element	Range of contents in gas condensate mg / liter (mean)	In exhalation, tons*	Percentage of content in magma†
Sb	0.021—120.7 (16)	2.8·10 ³	48
Cd	0.4—2.9 (1.07)	191	21
Au	7.6·10 ⁻⁶ —8.7·10 ⁻² (1.4·10 ⁻²)	2.5	14
As	0.001—24 (8.3)	1.5·10 ³	9.1
Hg	8·10 ⁻⁴ —0.111 (6.3·10 ⁻²)	11	3.1
Zn	0.67—113.4 (33)	5.9·10 ³	2.3
Pb	0.08—4.1 (1.42)	254	1.6
Sn	0.03—0.3 (0.15)	27	0.21
Cu	0.02—16.96 (6.4)	1.1·10 ³	0.18
Ag	6.7·10 ⁻⁴ —1.2·10 ⁻² (3.4·10 ⁻³)	0.6	0.16
Ni	0.023—1.2 (0.36)	64	0.02
Cr	0.07—1.5 (0.39)	70	0.01
Co	3·10 ⁻³ —5.8·10 ⁻² (1.8·10 ⁻²)	3	0.0021
Fe	0.5—48.2 (32)	5.7·10 ³	0.0012
Mn	0.22—0.48 (0.36)	64	0.001
Ti	0.16—2.4 (1.18)	211	0.0007

*Mean contents calculated per 1.79×10^8 metric tons of H₂O.

†Calculated from mean content of elements in 3.8×10^9 metric tons of basalts in GFTE.

tions of elements in the gas phase and the basalts allowed the authors to estimate the proportion removed from the primary magma, and thus determine the volatility or mobility of elements in their transition from the melt to the gas phase.

Table 3, based on data of [11], is descriptive of the scale of metal transport with exhalations and the degree of metal extraction from the magma in volatile compounds. The authors stipulate that the estimates of the amount of metal extracted from the magma are tentative, but the orders of magnitude are realistic or at least sufficient for gauging the scale of the transport and, above all, the geochemistry of the volatiles.

An analysis of the published data indicates that most volatile among metals are Sb, Cd, As, Hg, Zn, Pb, Au, while Cu, Sn, and Ag are also quite volatile; the less mobile elements in the magmatic process are Co, Ni, Cr, and Ti, and also Fe and Mn.

Detailed studies of the posteruptive processes in Greater Tolbachik volcano showed the exhalation mineral phases also to have high concentrations of Cu, Zn, Pb, As, Hg, Ag, Au, Sb, Sn, Cd, and low Ni, Co, and Cr [12], with the highest values recorded for Cu, Zn, and Pb [10]. Similar sets of elements have been discovered in sublimates of eruptive gases from many volcanoes of the world.

In [12] it was suggested that the source of metals enriching the volcanic exhalations are magmatic fluids of basaltic melts, evidenced by the precipitation of metal-rich mineral phases immediately after eruption close to the hot gas jets. The fluid source of metals is confirmed also by the ratios of one-forming elements in fresh and metasomatically altered basalt: in the latter, metal contents are usually higher than in unaltered rock.

The similarity of the associations of chemical elements in gas-condensate of basalt eruptions and their volcanic sublimates, the thermal solutions, and the sulfide accumulations of rift zones all indicate the important role of magmatogenic (fluid) source of metals in the process of hydrothermal-sedimentary ore formation.

This hypothesis accounts for various traits of the geochemistry of ore accumulations on the oceanic floor.

For example, the above-mentioned absence of nickel in thermal solutions and hydrothermal-sedimentary sulfides, contrasted against its high contents in basalts, can be correlated with the fact that nickel concentration in magmatogenic fluids is also low. The amount of nickel brought out by the Greater Tolbachik eruption was almost by two orders of magnitude lower than that of zinc, 18 times lower than copper, and three times lower than cadmium.

It is possible that the chemical properties of nickel, such as the high melting point of its silicate compounds and high affinity with sulfide ore, are conducive to release of this element into the solid phase during the early high-temperature stages of melt crystallization, preventing the element from passing into fluid. As a result, nickel contents in thermal solu-

tions and the sulfides precipitating from them are very low, while the magmatic sulfides as such are enriched in this element.

The behavior of zinc in magmatic process is also indicative. In [51] it was shown that Zn passes into sulfide phase during magma crystallization less easily than other elements, because of its low affinity with sulfide sulfur. This is confirmed by the nearly total absence of magmatic Zn sulfides in oceanic basalts. On the other hand, zinc with other volatiles is present in substantial amounts in the fluid phase, which is responsible for the high concentrations of this metal, both in thermal solutions, and in hydrothermal-sedimentary deposits of the ocean floor.

Not all of the highly volatile elements that are actively brought out of the magma by exhalations are accumulated in the solid phase of the sediment. These are, for example, Hg, Sn, and Sb.

In Recent sulfide ore shows, and in ancient pyrite deposits, a geochemical zonality is observed, which generally corresponds to this sequence of element accumulation from the discharge source to the deposit perimeter: $\text{Cu} \rightarrow \text{Zn} \rightarrow \text{Pb}$ [25, 34, 45, etc.].

With special reference to the distribution of elements in the sulfide deposits of the Red Sea, the authors of demonstrated that the geochemical zonality, determined by the sequence of precipitation of sulfides, is controlled largely by the stability of chloride complexes of metals in the solution.

The absence of low concentration of certain volatiles in sulfide deposits of the rift zone could be attributed to the higher stability of those complex compounds in which they are transported; this stability will lead to a high migration capacity, so that the elements could be transported in dissolved state over large distances from the source.

Experiments and thermodynamic calculations have shown, for example, that mercury transport in metalliferous hydrothermal solutions can occur both in chloride and in hydrosulfide complexes, depending on the concentration of H_2S in solutions. Temperature and acidity variations do not affect the precipitation of mercury [23], which determines its usual low concentration in oceanic hydrothermal sedimentary sulfide formations.

For other elements (such as Sb and Sn), the reasons of their low concentration in ore deposits, despite high volatility, remain unclear. One possibility is that the small amount of tin in sulfide accumulations could be due to the form in which this element is transported as part of stable sulfide complexes. This surmise is confirmed by correlations between the various components of gas condensate samples from Greater tolbachik eruption. Calculations showed that ore-forming metals correlated positively with Cl and usually negatively with sulfur; the sole exception was tin (correlation coefficient of Sn with chlorine is -0.5, with sulfur +0.841).

Little is known about Sb distribution in oceanic metalliferous sediments. Judging by the few published determinations (see Table 1), Sb concentration in sulfides is above its average content in oceanic basalt.

Generally, the geochemical specialization of hydrothermal-sedimentary and especially sulfide deposits in the rift zones appears to be controlled by the behavior of the heavy metals in the magmatic process. The participation of the fluid in the thermal solutions may determine not only their temperature regimes, but also the metallogenic functions, and affect also the acid-alkaline properties.

The hypothesis of the role of magmatogenic fluids as determining the pH of the thermal solutions is based on calculations with a model of formation of hydrothermal solutions as seawater interacts with oceanic basalts [30]. It has been calculated that pH of seawater equal to 7.8 is gradually lowered in the course of hydrothermal lixiviation of basalt, from 6.38 at 100°C to 5.67 at 350°C. It is known, on the other hand, that the high-temperature hydrothermal solutions are much more acid: the measured pH at 350°C is usually 3.4-3.6 (see Table 2). One possible reason for the discrepancy of real pH in thermal solutions and their calculated values could be the participation of ultra-acid magmatogenic fluids, with pH usually <1.

The enrichment of ore sediments in heavy metals is largely controlled by the relationship between the volatility of elements and the stability of their migrational complexes.

From an analysis of the real distributions of chemical elements in Recent thermal solutions and hydrothermal-sedimentary deposits of the oceanic crust, combined with the data on the composition of oceanic basalts and gas condensate of volcanic eruptions, it is possible to conclude that the magmatogenic sources play an important role in forming the sulfide mineralization of rift zones of the world ocean.

A magmatic origin of metals in ore-forming solutions, which were the source of deposits such as Kuroko (Japan), is assumed by most Japanese investigators [44, 47, etc.]. This view is also shared by many Soviet geologists, who investigated pyrite deposits of the Urals and the Caucasus [17, and others].

While acknowledging the importance of magmatogenic, fluid source of metals, the interaction of solutions with enclosing rocks should not be overlooked.

The influence of these processes on the formation of the principal salt background of solutions has been examined in [6]; it is more difficult to evaluate the role of crustal basaltic component in the supply of the ore-forming metals. As noted, laboratory experiments do not clarify this issue. A comparative analysis of the composition of gas condensates and thermal solutions from rift zones suggests that basalts had a major part to play in supplying ore elements, such as Fe, and especially Mn. These elements are the bulk of metalliferous oceanic sediments, and exhibit highest concentrations in ore-forming solutions of the rift zones as well (see Table 2).

On the other hand, the amount of Fe carried by volcanic exhalations is comparable with that of Zn and Cu, while the quantity of Mn is much lower than that of sulfide-forming metals (see Table 3).

The high iron, and especially manganese, levels in thermal solutions after their interacting with enclosing rocks, as compared with the primary magmatogenic fluid, are apparently due to extraction of these elements from oceanic basalts. While the behavior of minor elements in laboratory experiments is uncertain, iron and manganese are usually intensely washed out of basalts in course of their hydrothermal lixiviation.

A comparative analysis of ample factual data on the geochemistry of hydrothermal-sedimentary ore mineralizations of the world ocean floor, the chemical composition of thermal solutions discharging on the seafloor, and volcanic gas condensates, as well as in vitro experimental findings, suggests that the ore-forming metals have multiple sources in hydrothermal-sedimentary oceanic ore formation. The main sources are magmatogenic gas-water fluids and oceanic basalts, with each source playing a different role for each element.

While those metals concentrating mainly in sulfides are brought largely with the fluid phase of magmatic melts, in contrast, iron, and especially manganese, are derived mainly from interactions of solutions with oceanic basalts.

Generally, the ore-forming thermal solutions of the rift zones of the world ocean are highly complex, polygenic physical-chemical systems. The formation of their composition and its alterations as the solutions circulate through cracks in basalts are controlled by a large range of parameters: the physicochemical characteristics, the temperature, the water-rock ratios, the oxidative and acid-alkaline properties of solutions, their flow rates, and the crystallochemical properties and stability of mineral phases. Many of these parameters seem to be determined largely by the participation of magmatogenic-fluid phase in the hydrothermal solutions.

Some of the aspects of the complex and multifactorial process of hydrothermal-sedimentary ore formation remain obscure. The present level of our knowledge is insufficient for quantitative evaluations of the contributions of the various sources or for identifying all the factors at play.

Generally, understanding the sources of material in hydrothermal-sedimentary ore formation requires a comprehensive analysis based on a combination of an overall geologic and tectonic investigation with detailed studies of geochemistry, mineralogy, isotopic data, and physical-chemical properties of both the ore-forming solutions and the metalliferous deposits formed in their discharge areas.

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A study has been made of the distribution of uranium and thorium and the correlation relating them to other elements in the ferromanganese nodules of the Pacific Ocean. It has been shown that the uranium and thorium in the nodules is found in finely dispersed, probably sorbed form; the characteristic mineral phases of uranium and thorium were not detected in an electron microscopic study. It is proposed that uranium and thorium accumulate in the nodules by the diagenetic mobilization of the bottom sediments.

The distribution of uranium and thorium in ferromanganese marine nodules is of interest in connection with the general questions of the geochemistry of these elements in seawater and with the problem of dating the nodules using the methods of absolute geochronology based on the radionuclides of the uranium and thorium series.

Systematic studies of uranium and thorium nodules have generally been limited to the mid-Pacific Ocean [23, 25, 28]. For this reason these elements have been determined by us in nodules and metalliferous crusts collected in different parts of the ocean and differing in composition and conditions of deposition.

The samples studied are represented by samples from three categories: nodules from the equatorial North Pacific nodule belt (the radiolarian belt, or the Clarion-Clipperton fault zone), nodules from the southern regions of the Pacific and Indian Oceans, and ferromanganese crusts from the Mid-Pacific Ridge (North Pacific).

The samples from the Mid-Pacific Ridge were collected by one of the authors during the 48th expedition of the research vessel *Vityaz'*; the remainder of the samples were collected by members of the P. P. Shirshov Institute of Oceanology during several expeditions of the research vessels *Vityaz'*, the *Dmitrii Mendeleev*, and the *Academician Mstislav Keldysh*.

A detailed description of the depositional conditions, the mineralogy, and the overall chemical composition of the ferromanganese nodules and crusts studied is given in [6, 12].

From each specimen an average bulk sample was prepared for all the different methods of analysis. From seven specimens, samples were taken from the outer crust or from its upper and lower parts and the core. Three average samples were also analyzed that consisted of several dozen nodules totaling 6-8 kg that represented the material from the radiolarian zone, the Southern Basin, and the seamounts of the Pacific.

The uranium and thorium were determined by an x-ray spectral method, and all the other components (Fe, Mn, T, etc.), by chemical and atomic absorption methods. The distribution of the uranium was studied by electron microautoradiography and microdiffraction [2, 4].

The content of the uranium in the ferromanganese nodules and crusts studied varied from <5 to 22 g/ton, the content of thorium from <5 to 63 g/ton (Table 1).

The lowest (<5-15 g/ton) contents of uranium were determined in ferromanganese nodules from the southern parts of the ocean. In the nodules from the radiolarian zone, the content of uranium is somewhat higher (from 6.3 to 18 g/ton). The highest contents (12-22 g/ton) of uranium are characteristically found for ferromanganese crusts from the seamounts.

The distribution of thorium is on the whole not related to the distribution of the uranium. Its lowest values (<5-21 g/ton) are found for the Fe-Mn crusts. The ferromanganese nodules from the radiolarian zone contain 7.6-32 g/ton thorium, and those from the southern zones, 15-63 g/ton.

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The most important generality concerning the chemical composition of the material studied is that the Fe-Mn nodules from the radiolarian zone are relatively impoverished in iron, cobalt, and lead, and enriched in manganese, nickel, copper, zinc, and molybdenum. The ferromanganese crusts containing more iron and less manganese are characterized by lower contents of aluminum, nickel, and copper, and elevated contents of cobalt and lead. The Fe-Mn nodules from the southern regions of the oceans occupy an intermediate position in this respect.

Analysis of the individual zones of the nodules showed that thorium invariably accumulates in the outer layers, its upper part, in contact with the bottom water, being enriched relative to the lower part in contact with the bottom sediment.

The behavior of uranium in this respect is variable. In three instances its relative accumulation in the cores of the nodules was established, in two, in the outer crusts of rounded nodules, in one case, in the upper part of the outer layers of a compacted nodule as well as in the lower part of the same nodule.

In two nodules (St. 1936 and 2483-16, divided into crust and core, the distribution of uranium was analogous to that of manganese and opposite to iron. In two other nodules (St. 666-1 and 2483-43), divided into upper and lower crust and core, uranium was also distributed similarly to manganese, except for the lower crust, where its content rose following manganese, and in the other, lower (for higher iron and manganese). In a nodule from St. 2473-32 a monotypic distribution of uranium, thorium, manganese, and iron is observed; in one from St. 5965, uranium and thorium follow iron, and in one from St. 2520, uranium does not correlate with either manganese or iron.

The behavior of thorium is more stable. In five of the nodules listed above it correlates with iron, in one, with iron and manganese (St. 2474-32), and in one, with manganese (St. 2520).

Analysis of the correlations among the elements (Table 2) reveals two associations. The first includes elements associated with iron: titanium, lead, cobalt, and thorium. Uranium may also be assigned to this group, as this correlates with cobalt and lead. The correlation between uranium and manganese is weak, and that with thorium is negative.

To study the form in which the radioactive elements are found in the nodules, electron microautoradiographic studies were performed. This method is based on the ability of the ionizing radiation from these elements to reduce silver bromide of photoemulsions applied to the surface of the sample to metallic silver, which is detected by the electron microscope in the form of dendritic crystals. The results of these studies showed (Figs. 1 and 2) that uranium and thorium do not form independent mineral phases, but are found in a finely dispersed, probably sorbed, form. This view is accepted by many other researchers, as well [5, 11, 18].

The contents of these elements in our samples is within the limits established by earlier researchers for similar materials (Table 3). Higher contents of uranium in Pacific Ocean nodules (6-40 g/ton) and in ferromanganese crusts (up to 47 g/ton) were reported in [13].

Three series of determinations of uranium were made earlier on the nodules of the radiolarian zone and showed a mean content of 1-13 g/ton [23, 25, 28]. The mean value obtained by us (10.7 g/ton) is thus intermediate with respect to the earlier values. On the basis of the data in Tables 1 and 3, the mean content of uranium in the ferromanganese nodules of the Pacific Ocean is 7.5 g/ton, in the nodules of the radiolarian zone, 9 g/ton; in the nodules outside the boundaries of this zone, 7 g/ton; and in the ferromanganese crusts from the Mid-Pacific Ridge, 17 g/ton.

The content of the thorium in the ferromanganese nodules of the Pacific was determined earlier by several research groups [10, 11, 13, 19-22, 25, 28]. These values range from 2.8 to 154 g/ton. Kunzendorf and Friedrich [20-22] established the most narrow (21-36 g/ton) limits for the variability of thorium content in nodules, but in individual nodule belts they detected high (to 130 g/ton) values for its concentrations.

The content of thorium in the nodules of the radiolarian zone, from the data of a number of researchers [25, 28] varies within limits of 9 to 38.4 g/ton and has a mean value of 21 g/ton (cf. Table 3), which is in agreement with our data (cf. Table 1).

TABLE 1. Chemical Composition of Ferromanganese Nodules and Their Uranium and Thorium Contents.

Station number	Coordinates	Depth, m	Type of sample	Fe ₂ O ₃	MnO ₂	Al ₂ O ₃	P ₂ O ₅	TiO ₂	Ni	Cu	Co	Zn	Pb	U	Th
Radiolarian zone, northern tropical part of the Pacific Ocean															
666-1	14°23' N 117°19' W	4125	Radiolarian ooze	3,25	0,73	11,09	0,40	—	0,019	0,004	0,004	—	—	<5	12
			Compacted nodule	8,23	45,09	4,60	0,48	0,42	1,22	0,95	0,13	0,154	0,031	11	12
			The same, upper part	8,54	43,42	4,14	0,68	0,48	1,10	0,80	0,10	0,137	0,030	10	12
			The same, lower part	8,23	43,40	4,14	0,61	0,47	1,03	0,70	0,13	0,128	0,032	12	10
			The same, core	4,75	50,73	4,65	0,47	0,28	1,26	0,92	0,06	0,204	0,018	11	10
666-12	14°27' N 117°18' W	4065	Compacted nodule	9,44	42,78	4,86	0,66	0,49	1,23	0,86	0,19	0,142	0,042	13	14
1936	9°50' N 146°26' W	5200	Concreted nodule	17,72	33,72	3,49	0,76	1,55	0,85	0,42	0,34	0,070	0,082	11	32
			The same, crust	10,62	33,72	3,85	0,68	1,67	0,75	0,36	0,35	0,067	0,088	11	39
			The same, core	17,40	38,24	4,72	0,86	1,50	0,98	0,49	0,31	0,080	0,075	18	21
2520	10°28' N 175°07' W	5400	Smooth, rounded nodule	14,88	28,18	5,16	0,70	1,35	0,60	0,45	0,27	0,069	0,078	10	25
			The same, crust	14,90	34,22	3,41	0,67	1,36	0,91	0,67	0,29	0,094	0,079	8	28
			The same, core	14,56	22,64	5,08	0,73	1,30	0,32	0,24	0,21	0,043	0,085	9	14
2474-16	10°29' N 175°09' W	5260	Compacted, knobby nodule	14,14	30,26	5,23	0,51	1,14	0,85	0,53	0,24	0,068	0,054	6	20
2474-39	10°29' N 175°09' W	5260	Compacted, smooth nodule	13,92	39,03	4,36	0,75	1,26	0,96	0,58	0,28	0,087	0,068	13	23
2474-32	10°29' N 175°09' W	5260	The same	18,03	35,62	—	0,83	1,31	0,85	0,51	0,28	0,080	0,072	10	23
			The same, crust	19,63	35,73	4,43	0,15	1,40	0,93	0,53	0,31	0,082	0,070	13	26
			The same, core	16,44	32,21	7,05	0,36	1,15	0,81	0,46	0,21	0,073	0,061	5	15
2483-16	10°02' N 146°28' W	5200	Compacted nodule	5,70	43,28	4,07	1,02	0,59	1,36	0,98	0,18	0,136	0,038	14	14
			The same, crust	6,96	42,27	4,07	0,23	0,62	1,38	0,90	0,17	0,149	0,043	11	17
			The same, core	6,01	45,30	4,87	1,12	0,66	1,21	0,85	0,15	0,184	0,042	13	7,6
2493-43	10°02' N 146°28' W	5200	Compacted nodule	7,60	40,77	4,72	1,10	0,80	1,25	0,77	0,16	0,131	0,046	11	18
			The same, upper part	10,37	38,21	4,05	0,92	1,09	1,16	0,69	0,23	0,104	0,052	11	22
			The same, bottom part	7,82	31,14	4,78	0,32	0,86	1,28	0,78	0,18	0,108	0,045	6	18
			The same, core	4,11	34,70	7,41	0,81	0,49	1,18	0,85	0,10	0,123	0,025	8	10
			Average sample	7,37	45,31	4,50	0,55	0,67	1,29	0,96	0,20	0,125	0,034	12	15

Southern part of the ocean															
1664	14°15' S 165°52' W	5400	Polynuclear concretions	18,88	11,20	9,10	0,64	2,26	0,17	0,16	0,13	0,041	0,047	<5	16
5965	22°41' S 160°50' W	4850	Spherical concretions, upper part	26,90	22,14	4,50	0,65	2,41	0,31	0,17	0,50	0,070	0,130	15	63
			The same, subcrust layer	22,47	23,16	5,96	0,77	2,10	0,45	0,20	0,45	0,064	0,095	12	34
			The same, core	20,89	24,66	5,81	0,75	1,94	0,30	0,11	0,49	0,050	0,094	11	32
			The same, av. sample	22,16	26,48	5,95	0,84	1,84	0,40	0,17	0,47	0,060	0,104	8	35
5201	22°25' S 91°39' E	5280	Spherical nodule	18,99	29,69	3,70	0,54	1,32	9,46	0,17	0,33	0,051	0,108	12	51
2754	60°00' S 167°28' E	4540	Round, knobby nodule	12,66	23,18	5,54	0,25	0,91	0,74	0,30	0,06	0,078	0,058	<5	27
2757	56°56' S 170°29' E	5350	Round, smooth nodule, metalliferous crust	22,15	20,13	2,98	0,65	1,22	0,23	0,07	0,15	0,046	0,120	5	58
2762	55°00' S 170°29' E	4865	Round, rough nodule, metalliferous crust	21,10	21,04	3,90	0,50	1,33	0,38	0,15	0,17	0,071	0,108	8	51
Seamounts of the North Pacific															
6002	20°41' N 170°32' W	1930	Metalliferous crust on frag- ments of hyaloclastites	21,52	27,68	2,11	1,71	1,91	0,34	0,06	0,65	0,053	0,177	17	11
6348	18°31' N 175°06' W	1050	Metalliferous crust on tuff-breccia	15,19	35,73	0,94	0,82	1,12	0,59	0,04	0,64	0,073	0,200	22	<5
6352	18°19' N 178°20' W	1630	Metalliferous crust on basalts	21,84	28,68	1,01	1,30	1,63	0,36	0,02	0,82	0,044	0,185	16	18
6358	18°37' N 171°08' E	2440	Metalliferous crust be- tween hyaloclastite and phosphatized limestone	20,57	23,66	1,52	5,52	1,71	0,22	0,12	0,32	0,059	0,197	14	15
6359	19°02' N 171°08' E	1300	Metalliferous crust on phosphatized limestone	7,60	29,19	0,29	10,78	0,88	0,70	0,11	0,34	0,087	0,102	12	6
6365	22°20' N 161°31' E	1220	The same	18,36	34,22	0,94	1,42	1,26	0,50	0,03	0,76	0,061	0,182	19	21
6366	22°39' N 160°52' E	1280	Metalliferous crust on hyaloclastite	22,15	30,69	1,31	1,41	1,36	0,35	0,02	0,66	0,051	0,191	19	21
			Average sample of metalliferous crusts	19,65	36,61	1,40	1,63	1,33	0,51	0,06	0,80	0,062	0,192	17	20

Note. Contents of the elements are given in percent, those of uranium and thorium, in $10^{-4}\%$.

TABLE 2. Correlation Coefficients among the Elements in the Ferromanganese Nodules and Crusts Studied

Mn	Al	P	Ti	Ni	Cu	Co	Zn	Pb	U	Th	
-0,72	-0,18	-0,05	0,89	-0,86	-0,83	0,63	-0,84	0,70	0,18	0,64	Fe
	-0,11	-0,13	-0,77	0,87	0,78	-0,24	0,83	-0,44	0,25	-0,51	Mn
		-0,55	0,02	0,20	0,39	-0,61	0,17	-0,71	-0,66	-0,06	Al
			0,01	-0,20	-0,33	0,22	-0,12	0,37	0,28	-0,29	P
				-0,79	-0,74	0,54	-0,80	0,55	0,11	0,53	Ti
					0,94	-0,55	0,86	-0,74	-0,10	-0,46	Ni
						-0,69	0,87	-0,84	-0,28	-0,39	Cu
							-0,56	0,86	0,70	0,10	Co
								-0,66	-0,05	-0,46	Zn
									0,61	0,19	Pb
										-0,20	U

TABLE 3. Uranium and Thorium Contents in Ferromanganese Nodules of the Pacific Ocean, Pelagic Sediments, and Seawater

Sample type	Uranium			Thorium		
	Concn. limits g/ton (mean)	No. of sam- ples	Ref- erence	Concn. limits g/ton (mean)	No. of sam- ples	Reference
Nodules of the ocean as a whole	3-13,3 (8)	54	[1]	21-36 (28)	119	[20, 21]
	4,2-10,1 (4,9)	119	[20, 21]	10-130 (30)	121	[26]
				2,8-154		[10, 11, 13, 13]
Nodules of the radiolarian zone Pacific Ocean	2-35 (13)	6	[25]	10-30 (20)	25	[25]
	1,0-8,6 (4,5)	41	[28]	9,0-38,4 (22)	41	[28]
	- (1,24)	13	[23]			
Pelagic sediments	0,1-8 (2,2)	657	[1]	- (7,7)	1500	[9]
				3,5-22,0 (11,8)	132	[3]
Oceanic suspended matter Seawater	0,2-2,1 (1,1)	40	[8]	0,1-1,3 (0,3)		[7]
	- (3·10 ⁻³)	-	[15]	- (1·10 ⁻⁷)		[15]

The thorium contents in the ferromanganese crusts from seamounts south of the Hawaiian Islands (three samples) proved to be higher on the whole than similar crusts from the Mid-Pacific Rise, and were equal to 26-64 g/ton [20], which corresponds to the elevated contents of thorium we detected in ferromanganese nodules from the southern parts of the oceans. According to our figures and published data (cf. Tables 1 and 3), the mean thorium content in the ferromanganese nodules of the Pacific Ocean is about 30 g/ton, in nodules of the radiolarian zone it is 21 g/ton, and in ferromanganese crusts from the seamounts of the Mid-Pacific Rise it is 14 g/ton.

The distribution of uranium and thorium in individual nodule belts has usually been studied in conjunction with radiometric determinations of their age.

From the data in [13, 19, 20], uranium in nodules is concentrated primarily in the upper crust or in the outer crusts as a whole [10, 11]. Having analyzed 50 microsections of a single sample, H. Kunzendorf and G. Friedrich [20] established that the upper layers of the nodule contained 6.3-8.3 g/ton uranium, the intermediate layers about 5 g/ton, and the lower layers about 3.4 g/ton, and the very lowest, those in immediate contact with the underlying sediment, 2.7 g/ton. In the ferromanganese crusts the uranium content proved to be relatively uniform. In the eastern parts of the equatorial hemipelagic zone of the Pacific Ocean, however, uranium is concentrated primarily in the lower parts of the nodules [16].

According to the data presented in [20-22], the microdistribution of thorium inside the nodules is characterized by a definite tendency to a relative enrichment of the upper layers in comparison with the lower. The upper layers of one nodule studied in detail by these authors contained 40-130 g/ton thorium, and the lower layers contained 20 g/ton. The same picture was observed in ferromanganese crusts, where the upper layers contained on the average 64 g/ton thorium, and the lower, 26 g/ton. The results obtained by us were similar (cf. Table 1).

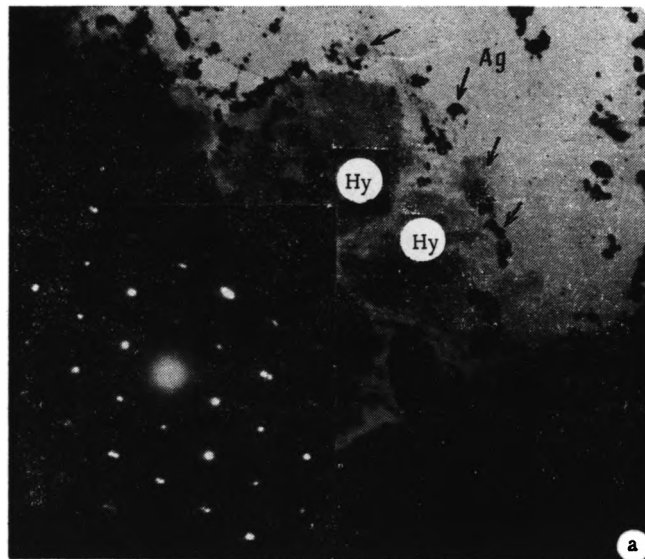


Fig. 1. Electron-microscope autoradiograph of the surface of a fragment of ferromanganese nodule. a) iron and manganese hydroxides (Hy) on which silver crystallites formed, marking the radioactive sites. Magnification 15,000 diameters; b) amorphous mass of iron and manganese hydroxides with uniformly distributed silver crystallites. Magnification 15,000 diameters.

The source of the uranium and thorium in the ferromanganese nodules may be, according to different authors [7, 10, 11, 13, 16-24, 27, 29], seawater, hydrothermal solutions, or the underlying sediments.

It is useful here to compare the contents of uranium, thorium, and the major ore-forming elements, iron and manganese, in nodules, sediments suspended matter, and seawater, which we have done on the basis of published data and our own data (Table 4). As we see, in the first three samples listed above these ratios are fairly close, at the same time differing markedly from those of seawater. It is evident that this is evidence that uranium and thorium do not enter the nodules by direct chemical precipitation from seawater. At the same time, the ratios in the nodules are closer to those of the sediments than to those of the suspended matter, with the exception of Th/Mn. Consequently, the diagenetic mechanism predominates for the incorporation of uranium in the nodules. Evidence for the diagenetic mobility of uranium in pelagic sediments was presented earlier on the basis of a study of its isotopic composition and behavior in pore waters [1, 17]. A comparison of the values of U/Fe and U/Mn in sedi-

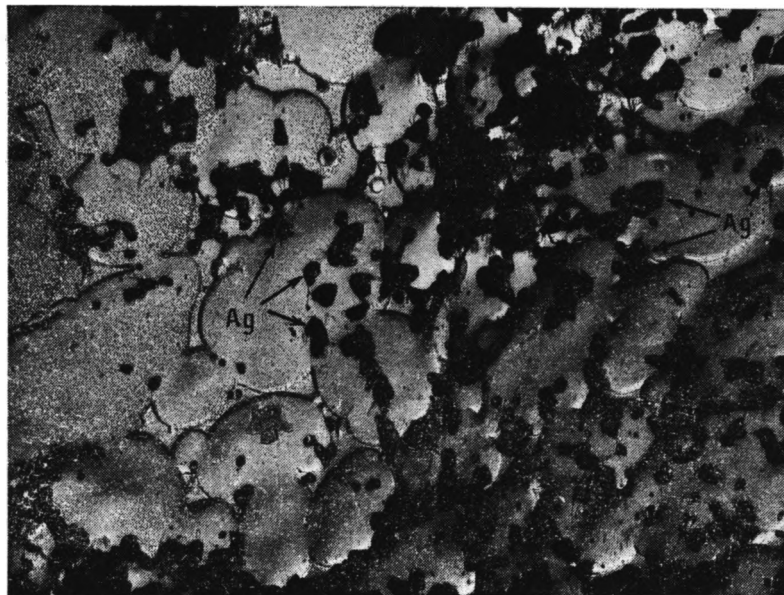


Fig. 2. Electron microscope autoradiograph of the surface of a fragment of a ferromanganese nodule with remains of microflora impregnated with iron and manganese hydroxides. Nonuniform distribution of silver crystal-lites. Magnification 15,000 diameters.

TABLE 4. Mean Ratios between Uranium, Thorium, Iron, and Manganese in Samples from the Ocean

Elemental ratio	Seawater*	Oceanic suspended matter	Pelagic sediments	Ferromanganese nodules and crusts		
				radiolarian zone	southern Pacific	submarine mounts
U/Fe	50	$0.3 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$
U/Mn	100	$10 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$0.3 \cdot 10^{-4}$	$0.4 \cdot 10^{-4}$	$0.8 \cdot 10^{-4}$
Th/Fe	$20 \cdot 10^{-4}$	$0.1 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$0.7 \cdot 10^{-4}$
Th/Mn	$40 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$15 \cdot 10^{-4}$	$0.7 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$
Th/U	$0.3 \cdot 10^{-4}$	0.3	3.5	2	5	0.8

*The data for U and Th are taken from Table 3, those for Fe and Mn, from [14].

†U and Th from [7, 8], Fe and Mn from [7, 8, 30].

*U and Th from Table 3, Fe and Mn from [9].

ments and nodules demonstrated that in the nodules the accumulation of uranium proceeds more intensively than that of iron and less intensively than that of manganese.

The behavior of thorium exhibits another peculiarity. The values of Th/Fe and Th/Mn in ocean sediments is approximately an order of magnitude higher than in suspended matter, apparently as a result of the dissolution of biogenic components (calcium carbonate and opal), which leads to the passive enrichment of the remainder in thorium. In the nodules the value of Th/Fe is in general the same as in sediments, which is evidence of their simultaneous accumulation. But the values of Th/Mn in nodules is 7-20 times lower for lower Th/U (0.8 on the average). In terms of the ratios U/Fe, U/Mn, Th/Fe, and Th/U, the ferromanganese crusts prove to be closer to oceanic suspended matter than the ferromanganese nodules, which is apparently evidence of the lesser degree of alteration of the sedimentary material on the undersea ridges than in the abyssal parts of the ocean.

* * *

The data considered allow the following conclusions to be drawn.

The mean contents of uranium and thorium in ferromanganese nodules from the Pacific Ocean can be estimated at 7 and 28 g/ton, respectively, and their accumulation coefficients relative to host sediments are 3 and 4, respectively.

The uranium and thorium in the nodules are distributed unevenly; they are found in a finely dispersed state and likely in sorbed form on iron hydroxides (Th, U) and to some extent on manganese hydroxides (U). They enter the nodules not by direct precipitation from seawater, but as components of particles of suspended matter and by diagenetic mobilization from host and underlying sediments.

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GEOCHEMICAL VARIATIONS IN PELAGIC SEDIMENT SEQUENCES.

INDICATORS OF BREAKS IN SEDIMENT DEPOSITION

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Geochemical features of pelagic sediments of the preequatorial Pacific zone are discussed with criteria for establishing the presence of unrecognized, short interruptions in sedimentation. Such an indicator is represented by Fe-Mn concretions that are enriched in Mn, Ni, Co, Cu and usually depleted in Zn and Cr, in comparison with background values. It is suggested that the value of the relative Mn-concentration index may serve as an indirect indicator of the duration of interruption in sediment deposition.

Each oceanic sediment type is characterized by only such a combination of basic components that reflect the influence of a complex of depositional processes. In sequences that include various sediment types, usually a regular pattern develops in the concentration changes of a series of elements. As the contrast between the composition of alternating sediments becomes greater, so sharpens the difference in their geochemical makeup. It might be thus expected that in lithologically uniform beds that represent only one sediment type, not subjected to the influence of endogenic sediment sources, the chemical composition would not vary greatly. However, extensive studies indicate significant geochemical variations in such beds. In the following, an attempt is made to relate certain findings in pelagic sediments of horizons that are enriched in ore components, to the very low sedimentation rates the essentially correspond to breaks in sediment accumulation.

The geochemical anomalies in lithologically homogenous sections have for long attracted the researchers' attention. Their nature has been interpreted in various ways. What appears to be the most elegant theory, involves diffusion flow of matter during diagenesis. The validity of these assumptions has been convincingly demonstrated, among others, through the study of element behavior at the boundary between reducing and oxidizing zones in sediment units in a trans-Pacific profile [6, 8, 16]. Numerous other examples of element migration under conditions of reductive diagenesis that is typical of ocean margin sediments, marginal and interior sea deposits. The consensus is that diagenesis in this region is driven by alteration processes in the organic matter.

Oxidizing diagenesis occurs in deep water pelagic deposits with small organic content (C_{org} : 0.1-0.3%) and physicochemical (colloidal) processes are dominant here [6, 11]. Unfortunately, the impact of oxidizing and suboxidational diagenesis [27, 28] has not yet been completely understood. Certain workers [31, 32, 33] indicated that in deep water deposits Mn migrates through pore water and is reduced from Mn^{4+} to Mn^{2+} , as organic matter and oxygen interact. Similar results were obtained in various Pacific Ocean areas [37]: Mn migrates from deep pelagic (oxidized) sediment horizons, is slowed down in the shallow subsurface (but not in the surface) layer and partially reaches the bottom waters through the sediment-water interface.

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TABLE 1

Station No.	Coordinates		Depth, in m
	N lat.	W long.	
2474-20	9°34.4'	152°39'	5016
2474-27	9°25.9'	152°40'	5356
2483-22	10°06'	146°26'	5043
2483-39	10°00.1'	146°29.5'	5136
2512-17	7°09.8'	172°53.1'	6006
2520-15	10°27.3'	175°11.6'	5323
2520-27	10°29.1'	175°07.5'	4945

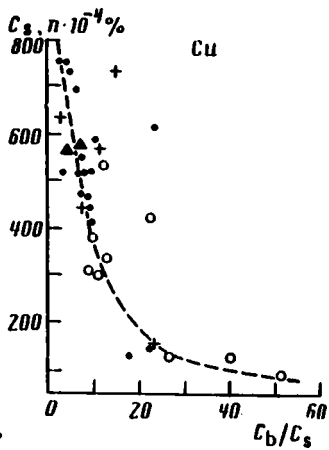
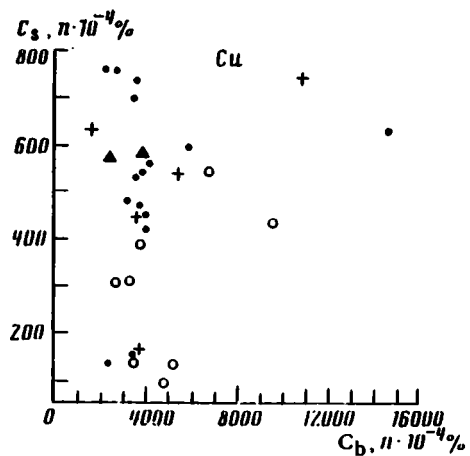
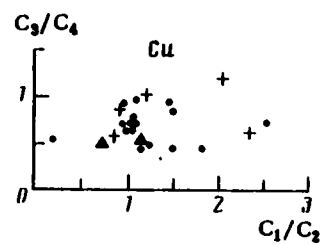
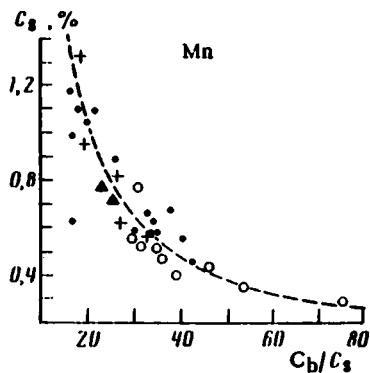
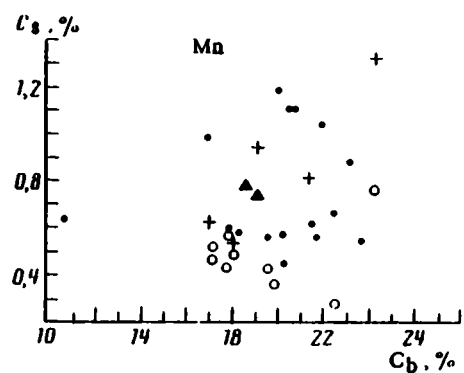
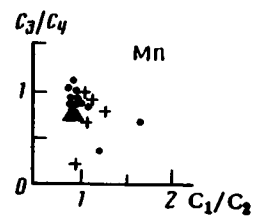
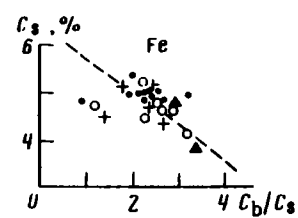
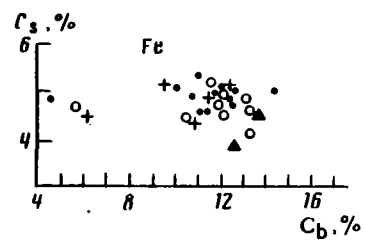
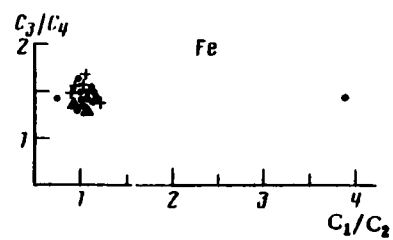
Within the uniform, 9.6-m-thick red clay core [37] the authors identified only one maximum of total and reduced Mn (30-35 cm horizon) in dry sediments. In pore waters the Mn content increases downward in the column. It reaches a maximum at 4-m depth, but in the sediments a relative concentration decrease occurs upward and downward from the maximum. In the suggested three-layered diffusional-advectional model of the vertical Mn distribution, the following patterns are predominant: The upper (oxidized) layer contain Mn ions that migrated through pore water, became oxidized and precipitated as Mn-oxides. In the intermediate layer with maximum Mn-concentration, the Mn ions and Mn-oxides don't change their chemical form because of the absence of appropriate energy input. In the lower, reducing layer the Mn-oxides become reduced to ions and are diffused through the pore waters. In general, the model assumes stable conditions throughout the time of sediment accumulation. For this reason, the boundary of the intermediate layer would migrate upward at the rate of sediment deposition, while the depth below the sediment-water interface is always fixed. In nearshore and pelagic deposits of various composition (red clays, limey and silica muds, turbidites, and blue silty clays) the lower bounding surface of the intermediate layer, enriched in Mn, occurs at 5-61 cm (maximum in red clays), while its thickness never exceeds 5 cm [37].

This model is tied to stable depositional conditions. It does not consider real geochemical inhomogeneities, caused by changes in depositional rates that may reach zero and interruption in sediment deposition. These may also be related to the local decomposition of biogenic matter, element reduction near traces of the biological activity of benthic organisms in sediment beds. It is known that reducing microenvironments around paths of mud-eating organisms lead to mobilization of Mn, Ni, Co; to a lesser extent of Cu. Iron is not influenced at all by reducing processes [24]. This element redistribution process results in a mottled discoloration pattern of cinnamon-brown pelagic sediments; eventually in chemical composition changes.

Certain workers [11] assumed that under weakly reducing conditions that exist in sediments, layers with higher Fe and Mn concentrations may form through burial of surface layers that are enriched diagenetically in these elements and in organic matter (C_{org} : 0.5-0.8%). Under satisfactory conditions, the surface layer becomes enriched in Fe and Mn. However, reverse reduction and "resorption" can not take place in the enriched layer at the rate of the burial, as it does take place in sediments with higher organic carbon content.

In all cited works, the geochemical inhomogeneities are explained by diagenetic redistribution of elements in the sedimentary layer and also by physicochemical processes at the sediment-water interface. The first attempts to tie lithological and geochemical anomalies to reduced sedimentation rates that alternate with episodic breaks in sedimentation and erosion, due to bottom currents, were in conjunction with the study of Mesozoic and Cenozoic Atlantic Ocean sediments [10, 29]. Based on direct observations and geochemical data, it has been assumed that the presence of red sediments in gray deposits is related to interruption in deep-water sediment deposition [10]. The presence of buried concretions and ore crusts in sediment beds in the Indian Ocean; of oxidized sediments in reduced beds [12, 13] was explained by reduced sedimentation rates. Such rates reached a zero value in given instances. These metals were found in high concentrations in sediments and concretions also in other parts of the world ocean, below the CCD and also in conjunction with breaks in sediment deposition [31, 38].

These examples essentially represent situations in which reducing and oxidizing conditions are mutually interrelated to different extent. In oxidized pelagic sediments the gamma spectrum does not conclusively reflect the geochemical inhomogeneities. There, the most important information comes from the analysis of change patterns in the concentration of various metals



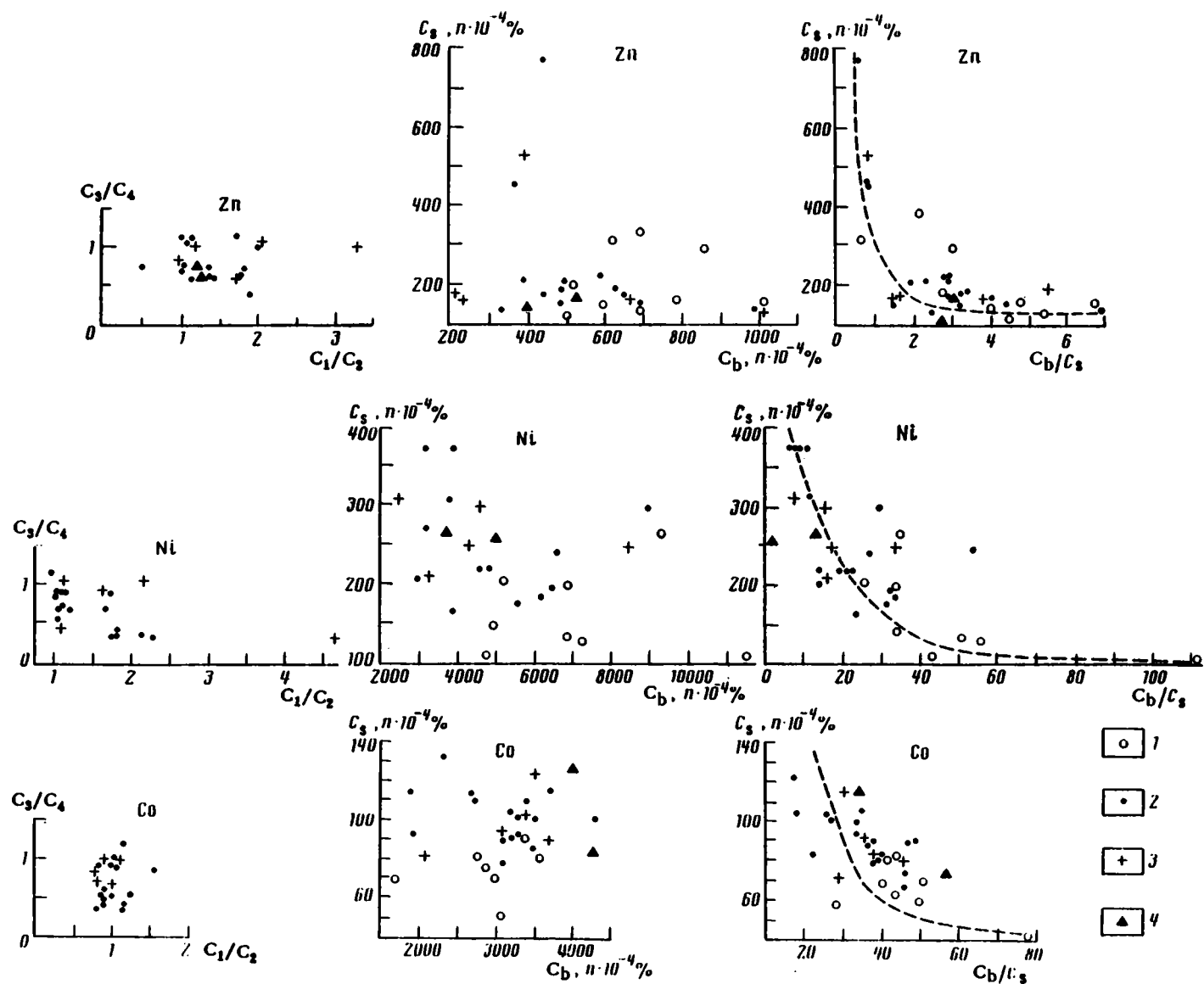


Fig. 1. Relationship of elements in the sediment-concretion system. Concretions in deposits: 1) surficial; 2) buried Pleistocene; 3) Pliocene; 4) Miocene. Element concentration. C_1 , ratio between surficial and buried concretion element-content; C_2 , in concretions, in general; C_3 , in sediments, in general; C_4 , ratio of element concentration in surficial concretions in buried concretions; C_5/C_b , ratio of element concentration in surficial in buried sediments.

TABLE 2. Coefficients of Relative Element Concentrations near Surfaces that Mark Interruption in Deposition

Station	Horizon, cm	Break *	Mn	Cu	Co	Ni	Zn	Cr	Fe	Al	Li	K	Pb
2474-20	20—25	HB	1,2	1,1	1,0	1,3	1,0	0,9	1,0	1,0	1,1	1,0	0,8
	120—125		1,6	1,3	1,3	1,7	1,3	0,8	0,9	1,0	1,1	1,0	—
	137—141	»	1,9	1,9	1,7	2,2	1,1	0,7	1,0	1,1	1,3	0,9	1,0
	145—150	HBC	1,8	1,0	1,7	2,2	1,1	0,7	1,0	1,1	1,4	1,0	1,0
	150—155	HB	1,9	1,9	1,7	2,4	1,1	0,7	1,0	1,1	1,4	0,9	1,0
	155—160		1,8	1,6	1,6	2,1	1,5	0,7	0,9	1,0	1,2	1,0	—
	160—165	HBC	1,4	1,5	1,6	1,6	0,9	0,9	1,0	1,0	1,1	1,0	1,1
	165—170	HB	1,4	1,5	1,5	1,5	0,9	0,9	1,0	1,0	1,1	0,9	1,3
	200—205	»	1,3	1,4	1,3	1,3	0,9	0,7	0,9	1,1	1,1	1,0	1,5
	320—325	»	1,3	1,4	1,1	1,2	0,9	0,5	0,9	0,9	1,1	0,9	1,6
2474-27	50—55	»	1,3	0,8	0,9	1,0	1,2	1,1	0,9	1,0	0,9	1,0	—
	180—185	»	1,3	1,0	1,1	1,3	1,3	1,1	1,0	1,1	1,0	1,0	—
	185—190		1,2	1,1	1,0	1,2	1,0	1,1	1,1	1,0	1,0	1,1	1,2
	280—285		1,4	1,0	1,1	1,5	1,3	0,9	0,9	0,9	1,0	0,9	—
	285—290	»	1,5	1,2	1,2	1,6	1,0	0,9	1,0	0,9	1,0	1,0	—
	315—320	»	1,1	0,9	0,9	1,2	1,3	0,8	1,0	0,9	1,5	0,9	1,1
	320—325	SIB	0,8	0,8	0,8	0,9	0,9	0,4	0,9	0,8	1,2	0,7	1,5
	330—335	HB	1,5	1,1	1,8	1,8	1,2	1,7	1,2	1,3	1,2	1,2	—
	335—340		1,3	1,0	—	1,4	1,2	1,0	1,2	1,2	1,2	0,9	—

2483-22	3--5	SIB	4,1	3,3	4,3	8,5	1,5	1,4	1,1	1,1	0,7	1,2	0,8
2483-39	95--100	HB	1,2	0,8	0,9	1,1	0,9	0,9	1,0	1,0	1,0	1,0	0,9
	272--277	"	2,4	1,3	1,8	1,1	1,0	1,1	1,0	1,0	1,0	0,9	1,0
	310--315	"	1,4	0,9	1,0	0,7	1,0	1,1	1,0	0,9	0,9	1,0	0,9
	475--480	"	1,6	1,1	1,1	0,8	1,1	1,1	1,0	1,0	1,0	1,0	1,0
	560--565	"	1,4	1,0	1,1	0,8	0,9	0,8	0,9	1,1	1,0	1,2	1,5
2512-17	10--15	"	1,2	1,0	1,0	1,1	0,9	1,0	0,9	1,0	1,0	1,1	0,7
	185--190	"	1,2	1,1	1,1	1,0	1,1	1,1	1,0	1,2	1,1	1,0	0,8
	450--457	"	1,2	1,0	0,9	1,2	1,1	0,8	1,0	1,0	1,0	—	—
	457--459	"	1,5	1,0	1,2	1,7	1,1	0,7	1,0	1,0	1,0	—	—
	525--530	"	1,1	1,0	0,9	1,1	0,9	1,0	1,0	1,0	1,1	1,0	0,8
2520-15	120--125	"	1,0	0,9	1,0	0,9	0,9	0,9	0,9	0,9	1,0	1,0	—
	125--130	"	1,1	0,9	1,2	1,1	0,9	0,9	1,1	1,0	1,3	1,0	—
2520-27	265--270	"	1,1	1,0	1,2	1,1	1,0	0,9	1,0	1,0	1,0	0,9	—
	270--275	"	1,1	1,0	1,1	1,2	1,1	1,1	1,0	1,1	1,1	1,0	—
	335--340	"	1,1	1,3	1,3	1,1	1,1	0,9	1,0	1,2	1,0	1,0	—

*HB Hidden break; HBC Hidden break, marked by concretions; SIB Stratigraphically indicated break.

in homogeneous portions of the section that is composed of but one sediment type. Such an analysis can distinguish stages of decreased deposition rates and associated short-term, hidden breaks in sedimentation. In contrast with apparent breaks, such hidden breaks often do not display macroscopically identifiable lithological features and they can not be easily defined by stratigraphic (micropaleontological, paleomagnetic and other) means. Only detailed geochemical studies of the sections can establish their presence. Examples of interpreted geochemical data for the purpose of identifying breaks in deposition are presented in the following.

The present paper is based on the study of 23 cores of oxidized pelagic sediments. The maximum 7 m long cores came from depths of 4788-6006 m from various Pacific Ocean quadrangles. They were taken during the 28th cruise of research vessel Dmitrii Mendeleev. Quadrangles 2474 and 2483 are in the western concretion-rich province of the Clarion-Clipperton area (NE Basin), quadrangles 2512 and 2520 in the Central Basin ore province; the Clarion quadrangle is located in the Clarion Fracture Zone. The sedimentary sequence was subdivided by V. V. Mukhina (diatoms and silicoflagellata), M. G. Ushakova (calcareous nannoplankton) and T. I. Lin'kova (magnetic stratigraphy). Atomic-absorption and chemical methods were used for identifying Fe, Mn, Al, CO₂, K, Cu, Ti, Zn, Ni, Co, Cr, Pb, Li, and organic carbon concentrations (analyses by N. P. Tolmacheva, E. S. Bazilevskaya, V. V. Gordeev, L. V. Demina, E. G. Sokolova, K. P. Tolok, and S. V. Khramov). About 600 samples were analyzed by various methods. Table 1 shows the locations of the most interesting cores that are discussed in the paper.

The samples to varying extent describe details of Middle Oligocene-to-Holocene sediments, including Quaternary deposits that across unconformities often overlie Paleogene and Neogene beds of various ages. Middle Oligocene radiolarian sediment and diatomaceous-radiolarian sediment underlie the correlated general section. The Middle Oligocene is overlain by Late Oligocene radiolarian sediments that include coccolithic-radiolarian layers with occasional Fe-Mn concretions and their fragments. The section is overlain by Miocene radiolarian, clayey-radiolarian, radiolarian-clay sediments and relatively compacted pelagic clays that display gradual intercalations. Locally, the clays are enriched in radiolarians; the lower units contain buried concretions. Radiolarian-clayey and clayey-radiolarian muds complete the sequence: concretions occur within the beds, as well as on the sediment surface. The average sedimentation rates during the last 0.7 millions years did not exceed 1.6 mm/1000 years in most of the quadrangles. Maximum rate was 5.5 mm 1000 years in the deepest quadrangle area, 2512.

In general, the studied areas contained abundant Fe-Mn concretions in the surfacial sediment layer (except for quadrangle area 2512). Buried concretions occurred in 60% of the cores. Mottled patterns, caused by the activity of benthic organisms and subsequent element redistribution processes were typical of the sediments. Almost everywhere, sediment genesis was accompanied by erosion and sediment redistribution. Sedimentation has been interrupted by pauses in deposition that lasted as long as several tens of millions of years. This situation also prevailed in adjacent northern-Equatorial zones of the Pacific Ocean [20, 26, 35].

It has been generally accepted that breaks in pelagic sedimentation resulted essentially from the low biological productivity of the surface waters and the transfer of sediments by fast bottom currents. These currents not only erode the bottom and redeposit the sediment but locally may even prevent settling of particles from the water even if the concentration of the suspension is significant in the water. On the bottom slopes such unconformities often are connected with gravitational processes. However, their identification is difficult when the transported matter is of small proportion. Nevertheless, redeposited sediments in depressions of the ocean bottom, associated with relatively steep slopes, serve as indirect evidence for the breaks. Such turbidite sediments, as a rule, differ from the enclosing deposits.

Conditions of "zero" deposition lead to formation of Fe-Mn microconcretions, concretions and crusts, "hard bottom" horizons, to the enrichment of surface sediment layers by Fe, Mn, and certain other "hydrogenic" elements by the sharp lowering of the nonore component (dilutant) concentration. The duration of the break determines how well these conditions are reflected in sediment composition.

The clearest display of geochemical inhomogeneities in the studied sediments occurred in local Mn, Fe, and associated trace element concentration peaks in concretions. Comparison of the metal concentration values in concretions and in the enclosing sediments (Fig. 1) indicates the absence of any regular relationships between them. However, with rate exceptions, concretions of a given time period contain more ore components than the enclosing sediments do: Fe: 2-2.5 times more, Mn: 17-80 × (30-80 on the surface), Cu: 3-50 × (13-50 on the surface), Zn: 1.4-7 ×, Ni: 8-60 (25-60 on the surface), Co: 15-80 × (27-80 on the surface).

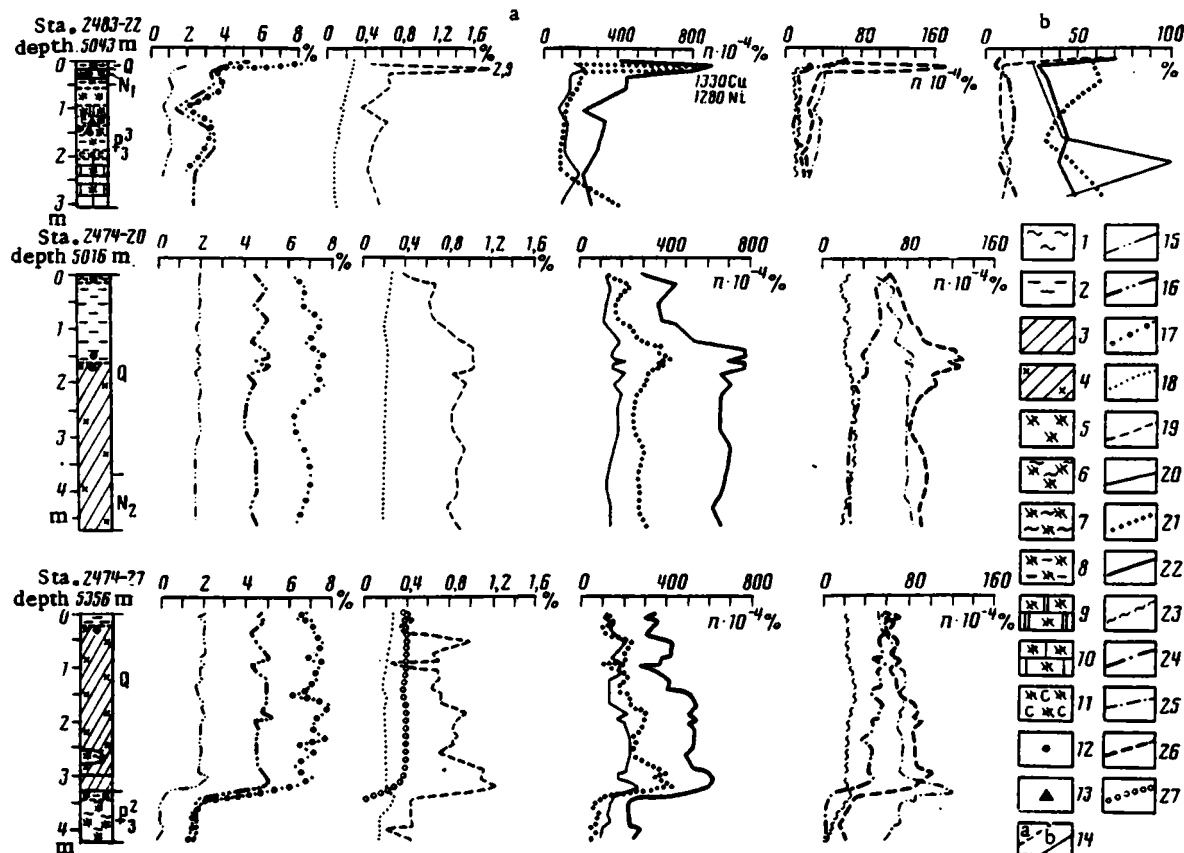


Fig. 2. Distribution of total concentrations and (a) fractions of mobile forms; (b) elements in pelagic deposits. 1) Clay-radiolarian muds; 2) radiolarian-clay muds; 3) miopelagic clays; 4) same, enriched in radiolarians; 5) radiolarian sediments; 6) same, enriched in diatoms; 7) diatom-radiolarian deposits; 8) clayey-radiolarian deposits; 9) coccolithic sediments, enriched in radiolarians; 10) coccolithic-radiolarian sediments; 11) radiolarian sediments with minor limey content; 12) Fe-Mn concretions; 13) fragments of Fe-Mn concretions; 14) boundaries (a - gradual; b - sharp); 15-27) element concentration curves: 15) K; 16) Fe; 17) Al; 18) Corg; 19) Mn; 20) Zn; 21) Ni; 22) Cu; 23) Pb; 24) Cr; 25) Li; 26) Co; 27) Ti.

The total amount of Fe and Zn in individual concretions was lower than in the sediments. These very elements behave independently of the age of the concretions, while the other calculated elements were significantly enriched in surficial concretions, in contrast with their concentrations in the buried ones.

If the ratio of metal concentrations in sediments (that enclose concretions) of the surface layer and of buried horizons in most instances approaches unity, then in surficial and buried concretions the concentration ratios often range between 0.7-2. The most ambiguous relationship between sediment and concretion composition exists when one correlates ore component concentrations in sediments with those in concretions and sediments (Fig. 1).

In using Fe-Mn concretions as basic diagnostic tools for recognition of hidden unconformities, one should broaden the concept that states that the formation periods of concretions correspond to times of decreased rates of pelagic sedimentation [1, 2, 7, 16]. Advocates of diagenetic colloidal-chemical concretion forming mechanisms [4, 5, 15, 16, 17, 18], assume that metal concentration in concretions occurs in the top c, 3 cm sediment layer, at 3 mm/1000 years sedimentation rate. If this is the case, one should admit the continuous formation of concretions in pelagic sediments. This, however is contradicted by the actual concretion distribution pattern in the sediment sequence. For this reason, admitting the depositional and depositional-diagenetic mechanisms of pelagic ore formation, Volkov [3] correctly indicated that a decisive rôle in the sharp geochemical changes in pelagic sediments, required for intensive ore formation processes, is played by the decrease in the absolute rates of sediment deposition. This occurs at the expense of nonore, terrigenous matter concentration,

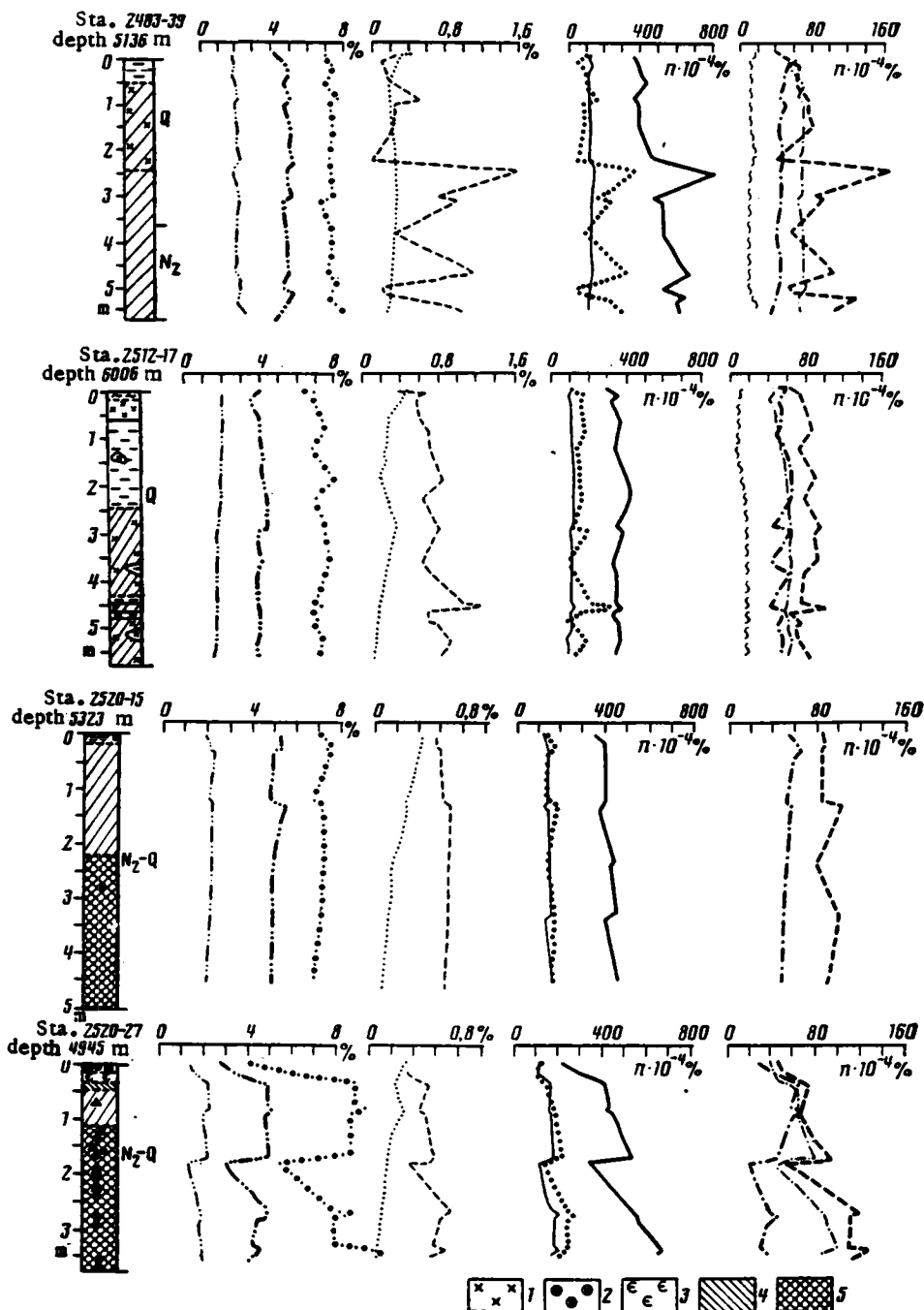


Fig. 3. Distribution of total element concentrations in pelagic sediments 1) clay-radiolarian muds; 2) coccolithic-foraminiferan sediments, enriched in radiolarians; 3) radiolarian-clayey, slightly limey muds; 4) miopelagic, slightly limey clay, enriched in radiolarians; 5) eupelagic clays. Other symbols, as in Fig. 2.

as the settling rates of the hydrogenic ore components remain practically the same. He included also the enrichment of sediments in all ore elements above the geochemical background level as a prerequisite for ore formation in pelagic sediments. The Mn-element subgroup enriches the sediments more than the geochemically less mobile iron subgroup does.

With regard to the above stated, [3] it appears that the most favorable conditions for the formation of ore concentrations in concretions and other geochemical inhomogeneities that are associated with breaks in sedimentation, are related to global climate changes and changes in bottom water circulation. However, contrary to the author's view [3], intensive ore formation was not restricted to Holocene times.

In particular, concretion distribution in pelagic Indian Ocean sediments suggests that even during the Quaternary they formed during several periods [12]. The same was found in other oceans [25].

A nucleation stage is required for the massive concretion development. This period probably coincided with times of increased ore element concentration in the surficial sediment layers. The concretion nuclei formed by tectonic, gravitational, chemical, biogenic and hydrodynamic processes. The hydrodynamic processes probably were decisive in preparing the nucleus and maintaining erosional conditions for extended time periods, as well as a "zero" deposition rate of the suspended material.

The asymmetry in the chemical composition of most pelagic concretions [36] suggests not so much their morphogenetic types [23], but their growth stages: not all concretions on the present ocean bottom surface can be considered "mature." Most workers believe that ore matter for concretion growth has been derived from sediments (early diagenetic matter) and from the water (sediment matter).

As known, during early diagenesis the driving force of metal migration, including that of Mn, is the microbiological disintegration of organic matter under aerobic conditions. In the Equatorial Pacific Ocean zones, the gradients of decreasing oxygen and organic carbon concentrations in muddy waters reach maxima in the top few centimeters of bottom sediments. At greater depths (10-20 cm), the system becomes stationary, as the disintegration and respiration of organic matter practically ceases [22]. Other data [34] show that the diagenetically active layer is 30-50 cm thick. The extent to which this layer participates in diagenetic metal redistribution is still unclear. Enrichment of the upper, semiliquid layer in ore components during diffusional ion migration of bivalent metals may be considered proof of the process [14]. This layer is the most instrumental in concretion growth. The diagenetic metal flux to the water-sediment interface is related in a complex and contradictory way with the deposition rates.

Each Fe-Mn concretion during an early or late stage probably goes through a diagenetic development phase. However, at optimum size of the pseudospheroidal core (few centimeters) the embryonic concretions occur mostly in the sedimentational stage in which the growth is determined by ore component flux from near-bottom waters. This mechanism is typical also of Fe-Mn crusts. The early sedimentation stage in concretion growth is the most favorable in interruptions in sedimentation. To the extent the normal depositional regime becomes influenced by reducing conditions, the contact between concretions and sediments increases. The diagenetic stage gradually takes over until mature concretions form immediately after concretion burial. All present concretions culminate their development in this stage. In the case of small or flattened concretion nuclei, a sedimentation stage probably does not occur. The depicted concretion growth sequence may often change if condition of sedimentation vary significantly. Various models, depicting the impact of sediment deposition conditions on concretion development have been detailed by Dietrich [21].

In addition to concretions, short-term breaks in sedimentation are indicated by ore element enrichment in thin horizons. An index of relative Mn-concentration (Table 2) was used to characterize such breaks. It is calculated from the ratio of concentrations in anomalous horizons (Fig. 2 and 3) and the mean content in corresponding sediment types in each quadrangle area (Table 3). To trace the dynamics of significant reduction in sedimentation rates, Table 2 displays data on sediments that under- and overlie anomalous horizons.

The results indicate the relative Mn-concentration index (K_{Mn}) in anomalous horizons of the studied cores does not exceed 4.1. As a base for comparison, the diagenetic maximum value for oxidized and reduced diagenetic types was of the order of 10-40 [19, 37]. The highest index values were found at the clearly displayed stratigraphic break of c. 10 million years duration (Stations 2483-22; Fig. 2a). The total Cu, Co, Ni, to lesser extent Zn concentrations sharply rose at the boundary. The conditions of decreased deposition were thus satisfied [3]. In this instance, these conditions meant a break in sedimentation. Very minor increases occurred in K, Fe and Al concentrations, while the Li and Pb did not reach background values. The ratio of mobile element forms (Fig. 2b) decreased at the same time at unconformity surface.

Stratigraphic breaks, however, cannot always be proven by geochemical data. In core 2474-27 (Fig. 2), the break at 320-cm depth is based on lithologic, micropaleontological and

TABLE 3. Average Element Concentrations in Quadrangle Areas

Sediment type	No. of map quad- angle	Organic	Al	Fe	Mn	Ti	K	Cu	Zn	Ni	Co	Cr	Pb	Li
Clay radiolarian mud	2474	0,36 (9)	6,7 (15)	4,6 (15)	0,46 (15)	0,37 (15)	1,89 (15)	370 (15)	148 (15)	155 (15)	69 (15)	58 (15)	20 (15)	59 (15)
	2483	0,37 (9)	6,6 (13)	4,7 (13)	0,54 (13)	0,33 (12)	1,87 (13)	417 (13)	163 (13)	197 (13)	57 (13)	54 (13)	19 (13)	59 (13)
	2512	0,34 (2)	6,6 (6)	4,1 (8)	0,62 (6)	0,29 (2)	1,83 (8)	358 (6)	112 (6)	149 (6)	76 (6)	59 (6)	18 (5)	47 (6)
	2520	0,34 (3)	7,9 (1)	4,8 (4)	0,44 (1)	0,37 (4)	2,20 (1)	310 (1)	168 (1)	145 (1)	78 (1)	52 (1)	Not det'd.	53 (1)
Radiolarian-clayey mud	2474	0,26 (5)	7,0 (43)	4,8 (48)	0,56 (48)	0,39 (31)	2,02 (44)	417 (44)	139 (44)	171 (44)	72 (43)	55 (44)	20 (41)	60 (44)
	2483	0,31 (3)	6,6 (12)	4,6 (12)	0,32 (12)	0,32 (8)	2,05 (12)	430 (12)	149 (12)	133 (12)	61 (12)	50 (12)	15 (12)	59 (12)
	2512	0,25 (3)	6,8 (11)	4,3 (11)	0,77 (11)	0,29 (1)	1,84 (10)	384 (11)	118 (11)	167 (11)	79 (11)	60 (11)	17 (8)	54 (11)
	2520	0,27 (11)	7,4 (8)	4,9 (7)	0,53 (8)	0,37 (7)	2,23 (6)	379 (6)	130 (8)	158 (6)	79 (6)	58 (6)	Not det'd.	54 (8)
Miopelagic muds	2474	0,21 (1)	7,1 (11)	5,0 (11)	1,06 (11)	0,33 (3)	2,09 (11)	673 (11)	215 (11)	341 (11)	96 (11)	43 (11)	19 (11)	73 (11)
	2483	0,27 (2)	7,3 (10)	4,8 (10)	0,68 (10)	Not det'd.	2,17 (10)	620 (10)	160 (10)	212 (10)	94 (10)	43 (10)	13 (10)	70 (10)
	2512	0,26 (1)	7,4 (4)	5,2 (4)	0,84 (4)	,	1,55 (4)	403 (4)	117 (4)	191 (4)	80 (4)	56 (4)	21 (4)	66 (4)
	2520	0,28 (7)	7,4 (22)	5,1 (26)	0,62 (22)	0,38 (8)	2,11 (20)	449 (22)	147 (22)	166 (22)	84 (22)	60 (22)	Not det'd.	70 (22)
Miopelagic clay	2474	0,19 (7)	7,2 (81)	4,9 (80)	0,73 (81)	0,40 (20)	2,00 (81)	520 (81)	170 (81)	241 (81)	82 (81)	46 (81)	10 (63)	73 (81)
	2483	0,21 (2)	7,4 (9)	4,9 (9)	0,44 (9)	0,35 (1)	2,04 (9)	473 (9)	151 (9)	149 (9)	84 (9)	48 (9)	14 (9)	70 (9)
	2512	0,26 (3)	6,9 (17)	4,5 (17)	0,89 (17)	0,29 (1)	1,67 (11)	377 (17)	119 (17)	182 (17)	82 (17)	55 (17)	25 (11)	63 (15)
	2520	0,33 (2)	7,7 (12)	5,1 (13)	0,56 (12)	0,40 (9)	2,19 (11)	426 (11)	136 (12)	144 (12)	84 (12)	58 (12)	Not det'd.	60 (12)
Same; enriched in radiolarians	2483	0,23 (2)	7,0 (7)	5,0 (7)	1,16 (7)	Not det'd.	2,28 (7)	711 (7)	181 (7)	386 (7)	109 (7)	30 (7)	17 (7)	66 (7)
	2520	0,14 (3)	8,0 (12)	4,7 (12)	0,66 (12)	,	2,04 (11)	528 (14)	168 (14)	214 (12)	101 (12)	43 (12)	Not det'd.	86 (12)
Clayey-radiolarian sediments	2474	Not det'd.	4,0 (3)	4,6 (3)	1,27 (3)	0,19 (3)	1,23 (3)	552 (3)	187 (3)	233 (3)	53 (3)	23 (3)	17 (3)	100 (3)
	2483	0,26 (2)	3,5 (7)	3,4 (7)	0,70 (7)	Not det'd.	1,02 (7)	400 (7)	156 (7)	151 (7)	34 (7)	21 (7)	13 (7)	71 (7)
Radiolarian sediment	2474	0,20 (3)	1,7 (10)	1,8 (10)	0,38 (10)	0,09 (1)	0,55 (10)	245 (10)	118 (10)	68 (10)	17 (9)	3 (10)	4 (4)	71 (10)
	2483	Not det'd.	4,7 (5)	3,5 (5)	0,97 (5)	0,25 (4)	1,30 (5)	529 (5)	167 (5)	336 (5)	55 (5)	30 (5)	18 (5)	56 (5)

Note. Concentration of organic C, Al, Fe, Mn, Ti, and K shown in percentages; that of remaining elements: in $\times 10^{-4}\%$. Number of samples in parentheses.

paleomagnetic data. The interval represents a 25 million years time span. Significant increases in the ore components at unconformity surface have been determined by sharp changes in sediment types (a contact between Oligocene clayey-radiolarian sediments and Pleistocene miopelagic clays); that is, by the essential characteristics of various deposit types. In the clayey-radiolarian sediments, influenced by long-term erosion, the concentration values of most elements, except for Li, were lower than the background values (Table 2). The paradox is explained by the fact that the background values were calculated only on the basis of three samples. In all instances, such sediments in quadrangle area 2474 were directly overlain by Pleistocene muds, across an unconformity surface. Thus, statistical problems related to background values, artificially decreased the geochemical contrast an obvious sedimentation break. In an adjacent area (quadrangle 2483), similar sediments were characterized by lower mean concentration values of all elements (Table 3).

Hidden breaks, marked by Fe-Mn concretion horizons, have been found in a core at station 2474-20 (Table 2; Fig. 2). Such horizons were not analyzed at other locations. The concretions occurred in radiolarian-clay muds and miopelagic clays. In concretion-bearing sediments the index of Mn-enrichment had values of 1.4 and 1.8. The sediments also contained higher concentrations of Cu, Co, Ni, and Li. The Zn, Fe, Al, K, and Pb values were close to background figures, while the Cr concentration was significantly lower. Apparently, the Cr value was due to the fact that this element does not accumulate in pelagic sediments but, when oxidized to hexavalent form, re-enters bottom waters [9, 30]. This occurs most extensively during breaks in sedimentation. Based on high residual concentrations, it appears that the ore components that accumulated during times of interruption in deposition are only partially utilized during the diagenetic concretion growth stage. This may explain the numerous geochemical inhomogeneities within pelagic sedimentary sections as brief, concealed breaks in deposition. At the same time, geochemical anomalies indirectly indicate the presence of concretion horizons, not identified yet by sampling.

Hidden sedimentation breaks have been identified geochemically in all the studied quadrangle areas (Figs. 2 and 3, Table 2). The K_{Mn} values at the unconformity surfaces ranged between 1.1-2.4. This indicates that, apparently, they were brief phenomena. Among the other elements, Cu, Co, and Ni displayed steady accumulation patterns at the unconformity boundary, while Cr and Ni showed opposite tendencies. Fe, Li, Al, K, and Pb showed no well-defined trends. Typically, the transition from normal deposition to the break, and in reverse, is gradual. It probably occurs via a series of brief sedimentation breaks and reduced rates of deposition (unsteady sedimentation). This is shown by the trend of change in the index values of relative ore element concentrations (Table 2).

The data confirm that geochemical inhomogeneities in the studied cores can not easily be reconciled with oxidizing diagenetic stages. There is very little reactive organic matter in the sediments and no sharply defined horizons occur in a cyclic sequence, enriched and depleted in ore components with low K_{Mn} values. Sediments of high concentrations of Mn, Fe and associated trace elements formed primarily on the ocean bottom surface under conditions of unsteady deposition. Low sedimentation rates and near zero centigrade temperatures existed when ore components, that entered from sea water, were only very slightly diluted by nonore components. No significant changes occurred after burial. Unsteady deposition in the sections was detected to a depth of 10-40 cm, representing a time-span of c. 50,000-200,000 years. Concretion horizons were observed in these zones or sediments with unusually high metal concentrations. It should be remembered that the diagenetic peak values occur within less than 5 cm [37]. The exact identification of surfaces, associated with hidden sedimentation breaks is feasible only by a continuous geochemical study of the sections.

Thus, the patterns of element distribution in sections of monotypic pelagic sediments may reflect the degree of stability in sedimentation. Fe-Mn concretions are prime indicators of sedimentation breaks. The presence of concretions in the sediment beds is indirectly shown by geochemical anomalies in horizons found in the available cores. Such horizons correspond to hidden sedimentation breaks but are not related to diagenesis. This fact is important when mapping areas of buried concretions. The hidden sedimentation break surfaces (unconformity) are characterized by higher values of Mn, Ni, Co, Cu, sometimes also of Fe, Al, K, Li, Pb; while the concentrations of Cr and Zn are below background values. The unconformity surface is also marked by reduced ratios of mobile element forms.

Our data suggest that the concentration of practically all the cited elements especially of Mn and Ni increases as the time-span of sedimentation break increases. Low K_{Mn} in the

studied cores indicated the brevity of most hidden sedimentation break-time intervals. The duration of the break is indirectly indicated by the degree of maturity of the concretions, when the total thickness of the sediment layer that exists immediately next to a large concretion nucleus is taken into account. If the concretion growth stages repeatedly alternate, one should assume the existence of long periods of unsteady sedimentation against general background of low overall accumulation rates. In contrast with diagenetic element concentration conditions sediment enrichment in ore components at such unconformity surfaces is related to conditions in sediment deposition.

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SECONDARY ALTERATION OF QUATERNARY BASALTS IN THE RIFT VALLEY OF
THE REYKJANES RIDGE

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Secondary alteration of basalts in the rift valley of the Reykjanes Ridge were studied on the basis of data obtained on the fourth leg of the scientific-research vessel *Academician Mstislav Keldysh*, in which the submersible vessel "Pieses" was used. It was shown that hydrothermal activity is the main factor in the secondary alteration of basalt. Amorphous, poorly crystallized phases are formed: palagonite, iron-silica phases, chlorophaeite, and celadonite-like material.

In recent years many studies of secondary alteration of basalts have appeared. This is related to the great amount of rock obtained by the drilling vessel "Glomar Challenger" and numerous dredges operated from both Soviet and foreign research ships. However, the drilling technology available at present cannot sample the youngest basalts of the oceans, which are not covered with sediments, the basalts of the rift valleys, while the relatively gently dipping occurrence makes dredging difficult. As a result, there are practically no studies on the alteration of minerals in Quaternary basalts of the rift valleys. Knowledge of these processes is necessary for understanding a large number of problems, including an explanation of the role of alteration in the deuteritic stage.

Interest in these problems has increased as a result of discussions of the formation of microscopic amorphous material long known as chlorophaeite [5, 6, 8-12, 14, 17, 18, and others]. These discussions have a long history and have arisen again as a result of publication of [11, 12]. The term chlorophaeite was introduced into the literature in the last century to indicate isotropic or weakly birefringent green or orange traprock material. A detailed description of this form has been presented in [18]. It is an amorphous, pitchlike material, with a conchoidal fracture, which fills vesicles and fractures in various types of basic rocks and forms pseudomorphs after olivine and possibly orthopyroxene. In transmitted light it appears green and brown, isotropic, or rarely birefringent. It was noted in [18] that chlorophaeite is not a mineral species and has a variable composition, and it was assumed to have formed as a result of the effects of hydrothermal solutions on cooling rocks. Many investigators have expressed a similar view as to the origin of chlorophaeite [5, 10, 17, etc].

In opposition to this, it has been suggested that chlorophaeite is formed during the late magmatic deuteritic stage [8, 9, 14, etc.]. This concept was developed most fully by Simanovich and his coauthors [11, 12], who studied in great detail chlorophaeites in traprock from the Tunguska syncline (Triassic), North Timan (Devonian), and in basalts from DSDP 304 (Cretaceous). These authors believe that chlorophaeite formed as a result of congealing of hydrated segregates of the mother liquor.

The discovery of chlorophaeite in oceanic basalts [10, 12, 14] energized the discussion of the origin of chlorophaeite, and consequently the role of the deuteritic stage in mineral alteration in oceanic basalts. However, the widespread occurrence of chlorophaeite, as well as other neogenic phases, has so far been described in relatively old basalts, where the effect of many post-deuteritic processes is difficult to ignore. In order to resolve the problem of the role of the deuteritic stage on the alteration of basalts it is natural to turn to the study of the youngest oceanic basalts, those of the rift valleys.

An expedition of the Institute of Oceanology, Academy of the Science of the USSR, undertook an investigation of the rift valley of Reykjanes Ridge, in the region of latitude 58°N, during the summer of 1982. Two ships, *Academician Mstislav Keldysh* and *Rift*, and two "Pieses"

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submersible vessels took part in the study. Information gathered during this expedition, kindly furnished to the author by Yu. A. Bogdanov, forms the basis for this paper. The geology and geomorphology of the area of study has been described in [2, 7], so only a brief discussion of the geological setting will be presented here.

The rift valley is about 15 km wide (Fig. 1). The ridges which extend along its sides generally have steep slopes facing the axis of the rift and gentle slopes on the other side. Two extensive volcanic ridges are located along the valley bottom, with a sigmoidal shape in plan and oriented at an angle of 20-30° from the strike of the axis of the valley. The northeastern ridge is 3-5 km wide and 700 m high. The ridge has been traced for a distance of about 20 km in the study area. To the north it almost abuts the side of the valley, while its southern end is 4-5 km from the edge of the scarp. The top of the ridge is relatively flat. The western slope is steep and highly dissected, while the eastern slope is more gentle. The southeastern ridge has a similar form. Individual small, elongate hills are parallel to the ridges.

The ridges and sides of the valley are composed of low-potassium tholeiites. Since there are no sediments on the volcanic ridges described above, the basalts forming them are assumed to be Holocene in age. Individual small hills located along the sides of the valley, such as in the western trough, are also composed of Holocene basalts. Besides these there are basalts of Würm age, as determined by the basal layer of the overlying sediments. These basalts form the hills that parallel the trend of the valley.

The most abundant type of basalt discharge is from lava pipes of various shapes and sizes. In the northern part of the northeastern ridge, close to its crest, a hollow tube with walls 10-12 cm thick was found. Typical pillow lavas were also encountered, and locally lava flows.

The basalts are basically porphyritic with a phenocryst content of several percent. The phenocrysts are plagioclase and olivine, rarely clinopyroxene. Some non-porphritic varieties are also found. The texture of the rock, depending on the location of the sample in the lava pipe or flow, ranges from glassy in the marginal areas through variolitic and paniculate to intersertal in the center. Vesicles (mainly spherical, from degassing, up to 1 mm in diameter) generally make up 5 to (less commonly) 8 percent of the volume of the rock. In some varieties, especially in glasses from hollow lava pipes, the size of the vesicles may be greater. In such cases ellipsoidal cavities up to 3 cm across are found. In varieties with paniculate and intersertal texture, along with relatively large degassing vesicles there are small cavities with irregular shapes. They range from tenths to hundredths of a millimeter in size and conform in shape to the interstices in which they occur. Segregation vesicles are also found locally.

The young Holocene basalts that form the volcanic ridges and hills contain virtually no neogenic minerals. Amorphous iron-silica phases have been found in a few degassing vesicles in only one sample, glass from a hollow pipe.

The earliest stages of alteration are found in basalts of Würm age. Weak palagonitization was found in the zone of sideromelane glass, while iddingsite is developed as fine inclusions within or in the marginal areas of some olivine grains in the interior of the body. In addition, some interstitial vesicles are lined with chlorophaeite that is light green in transmitted light. The boundary between the chlorophaeite and the cavity in the center of the vesicle is irregular, with bumps and knots. Similar material was encountered in capillary cracks cutting the rock. It must be noted that palagonite, as well as iddingsite and chlorophaeite, are quite insignificant in Würm basalts and make up hundredths of a percent of the total rock.

Only basalts from the area of hydrothermal discharge on the east side of the main volcanic ridge have undergone substantial alteration. Hydrothermal activity has been established by the presence in the rocks of sintery crusts enriched in a number of elements (Fe, Mn, Cu, Zn) characteristic of neogenic mineral formation in hydrothermal systems of the mid-oceanic ridges [7], and also by the early lithification of the sediments overlying the basalts [13].

The outer parts of pillow lavas and flows are the most intensively altered. Pillow lavas are usually covered by a thin (0.1 mm), dense, manganic crust with a knobby, sintery surface that has a dull, resinous luster and a black color. The interior of the manganic crust is porous and has a lighter, brownish color. The impression is given that the outer, black part (the crust) was formed by the precipitation of sinter, while the inner, brownish part formed a substrate.

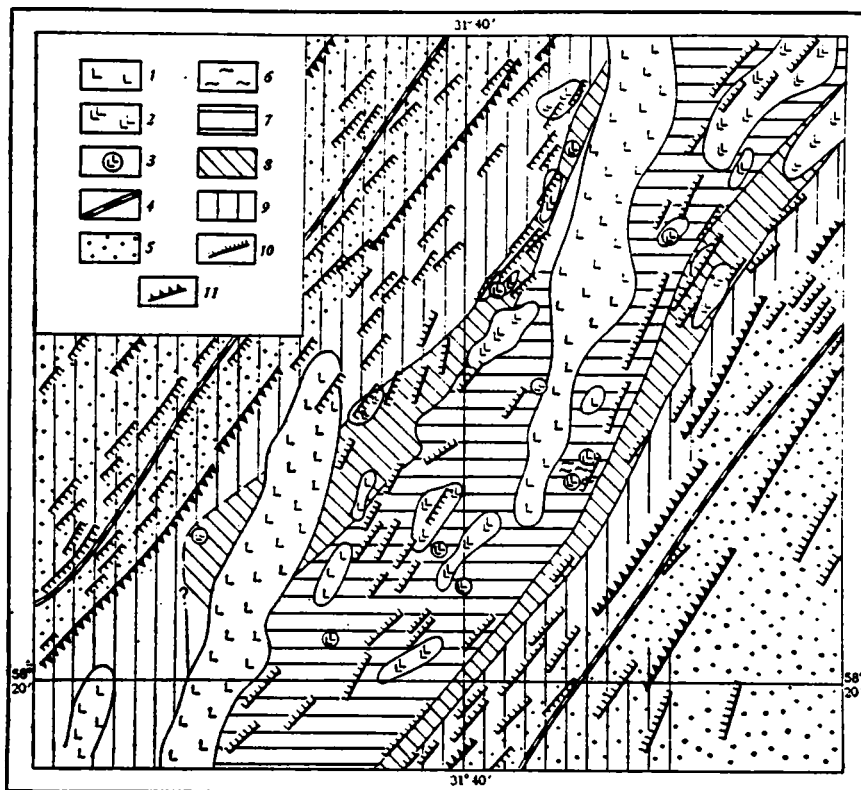


Fig. 1. Geologic map of the rift valley, Reykjanes Ridge [7]. 1-3) Basalts (1, Holocene; 2, Würm; 3, same, locally with a thin cover of sediments); 4) linear magnetic anomalies, corresponding to 0.97 ma; 5) tectonic scarp; 6) hydrothermal center; 7-9) thickness of sedimentary cover (7, less than 2 m; 8, 2-4 m; 9, more than 4 m); 10-11) faults (10, less than 300 m displacement; 11, more than 300 m).

Below the manganic crust is a zone of pure rock (up to 1 mm thick), and beyond that a zone of palagonitization (up to 5 mm thick), restricted to desquamational fractures and developed within sideromelane bodies in individual blunt, rootlike channels (hundredths of a millimeter thick). Palagonite is also formed along the boundary between sideromelane and plagioclase grains, and on the walls of fine degassing vesicles; less commonly it replaces sideromelane that is squeezed in between varioles. The palagonite is porous, ocher-colored, yellowish-gold in transmitted light, isotropic; the index of refraction ranges from 1.685 to 1.700; density is 2.6. The sideromelane in which the palagonite is developed is pale-cinnamon, translucent.

The chemical composition of palagonite from one of these rootlike channels, and of the sideromelane in which it is developed, is given in Table 1. "Sideromelane-palagonite" pairs from holes 407, 409, and 410, drilled on the slopes of the Reykjanes Ridge during the 49th leg of the voyage of the *Glomar Challenger*, are presented for comparison. The compositions of these pairs are characteristic for palagonites from oceanic basalts [6, 19]. The composition of the palagonite we studied is very different from that of the basalts in these core holes, although the trend of chemical rearrangement is generally the same. Most conspicuous is the heavy loss of silica and enrichment in iron. The concentration of iron, and also titanium and aluminum, may have been caused by depletion of material as a result of the loss of silica. The appearance of goethite, found as an admixture in x-ray-amorphous palagonite in the interior part of the zone of palagonitization, may be related to the high iron content. The variability of the chemical composition of palagonite has been noted by many investigators [3, 5, 18]. The differences in composition observed between the palagonite studied and those more typical of oceanic basalts is probably due to the composition of the hydrothermal solutions in which palagonitization took place in the rift valley of the Reykjanes Ridge. It should be noted that palagonitization with heavy loss of silica is characteristic of hyaloclastics of the submarine mountains of Atlantis, located south of the Azores [1]. Low-silica palagonite is also known in hyaloclastics of Iceland [4], although the silica content in these is somewhat higher (23%) than in our case (Table 1).

TABLE 1. Chemical Composition of Glass (a) and Palagonite (b) Pairs, Weight %

Oxide	1		2		3		4		5		6		7	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b
SiO ₂	52,88	14,23	49,04	39,95	49,46	43,15	49,63	39,39	49,99	36,94	50,69	33,58	47,95	23,48
TiO ₂	1,07	3,65	1,92	3,74	1,92	3,10	1,90	2,99	1,53	2,86	1,24	2,32	1,86	2,93
Al ₂ O ₃	13,93	20,63	15,69	10,71	14,05	9,91	14,48	11,63	13,26	7,02	16,61	17,40	14,42	20,55
FeO	11,15	35,03	11,93	20,38	12,61	19,36	12,11	17,39	12,25	21,65	7,97	12,23	12,41	19,95
MnO	0,22	—	0,15	—	0,22	—	0,22	—	0,21	—	0,14	—	0,19	0,26
MgO	7,64	3,48	6,23	2,97	6,52	3,32	6,61	2,63	6,10	5,50	7,12	0,99	7,13	0,80
CaO	11,78	2,20	10,93	1,94	11,42	1,78	11,24	1,45	11,38	0,66	11,00	1,61	11,90	0,84
Na ₂ O	1,87	2,09	2,49	0,93	2,48	—	2,60	1,89	2,13	—	2,80	1,85	2,16	0,14
K ₂ O	0,13	0,57	0,19	3,25	0,25	3,67	0,21	3,56	0,18	4,05	0,35	2,57	0,33	0,10
Σ	100,67	81,88	98,57	83,87	98,93	84,29	99,00	80,93	97,03	78,68	97,92	72,55	98,37	71,71

Note. 1, Sample P-104/16-6, rift valley, Reykjanes Ridge, "Kamebax" microanalyzer, G. V. Karpova, Geological Inst., Academy of Sciences of the USSR, operator; 2-6, from the 49th leg of the *Glomar Challenger* [19]: 2-4, hole 407, 5, hole 409, 6, hole 410; 7, sideromelane-bearing hyaloclastics, Iceland [4].

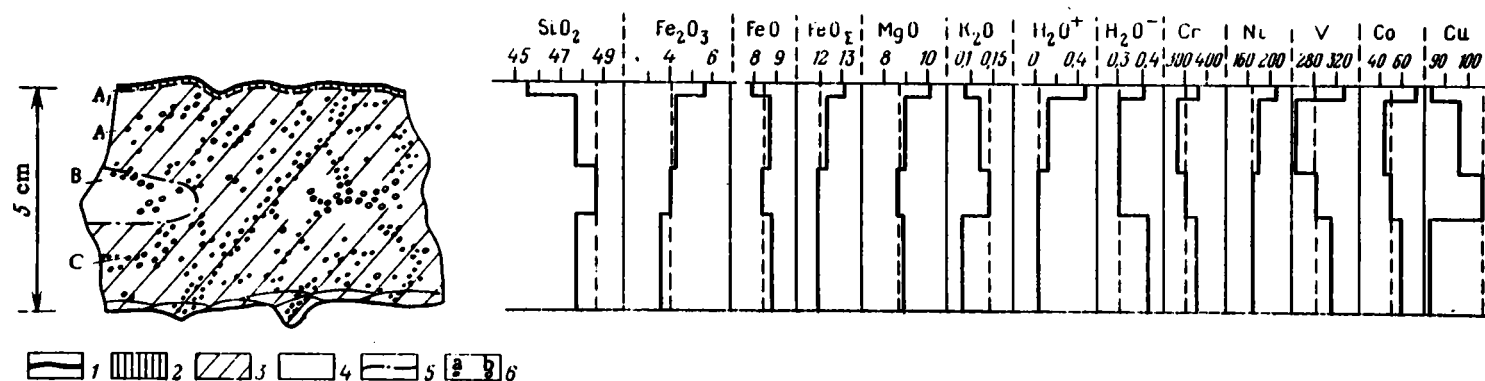


Fig. 2. Distribution of rock-forming and minor elements in a flow (sample 475). 1) Fe-Mn crust; 2) near-surface light-beige zone A₁; 3) marginal beige-gray zones A and C; 4) central blue-gray zone B; 5) "black front" line; 6) vesicles containing (a) and not containing (b) neogenic phases. Oxide content of rock-forming elements in wt. %, minor elements in g/ton. Dashed line, content in unaltered rock.

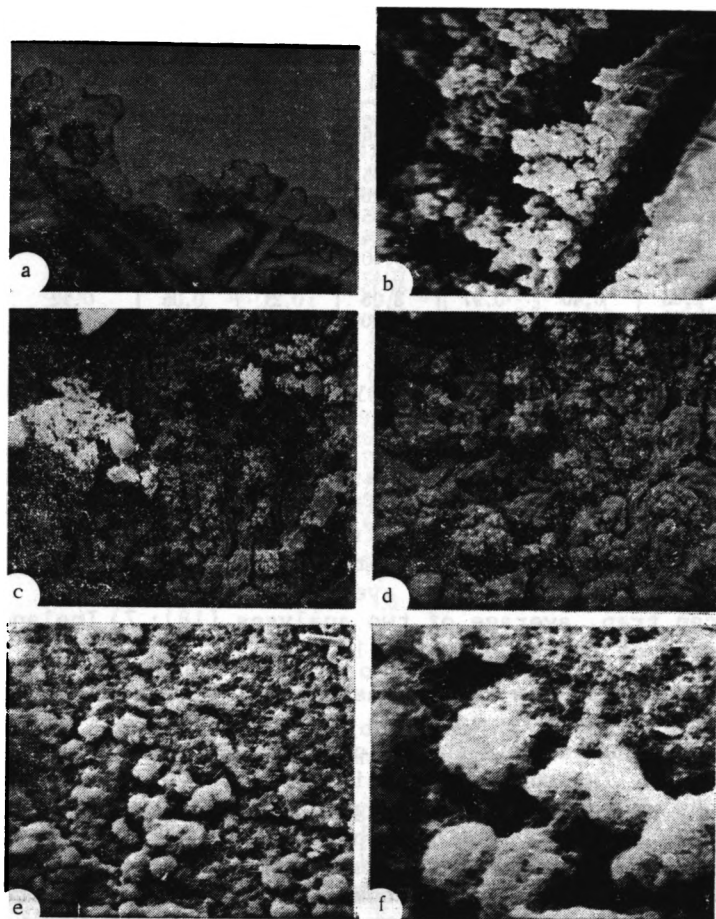


Fig. 3. Morphology of neogenic forms. a) Photomicrograph, $\times 100$, plane light; b-f) SEM ("Quick-scan," Moscow State Univ., V. M. Grigor'ev, operator): b) $\times 1000$, c) $\times 400$, d) $\times 800$, e) $\times 1500$, f) $\times 5000$.

Along with pillow lavas, thin lava flows were observed in the area of hydrothermal discharge. These flows were evidently formed from lavas that were rather liquid, with a low viscosity. How fragments about 6 cm thick were dredged at station 475.

The flows are non-porphyritic basalt with intersertal texture, changing to paniculate toward the margin of the flows. The rock is composed of fine, isometric grains of olivine (5%) and acicular or boxlike laths of plagioclase (An_{50}) (40-45%) between which are fine, locally elongated grains of clinopyroxene (up to 40%). Isolated areas are aphanitic or glassy, with scattered fine grains of ore minerals. About 5% of the total volume is vesicles. Spherical degassing vesicles up to 1 mm in diameter sharply predominate. They are irregularly distributed through the rock, forming trains at some points in the base of the flow (Fig. 2), which indicates appearance of a gassy phase at the point of extrusion onto the sea floor. Along with the large spherical vesicles in the groundmass, there are also fine, irregularly shaped vesicles.

Several zones can be recognized in a section across a flow according to the changes in color of the rock. The near-surface part of the flow (zone A_1), located directly below the thin manganic crust, is beige (up to 3 mm thick). Below this, zone A (up to 2.5 mm thick) is beige-gray, while the center of the flow (zone B) is blue-gray. Zone B is about 1.5 cm thick. The lower zone (C) is the same as zone A and has about the same thickness. In places zones A and C come together and zone B pinches out. The transition from zone B to zones A and C is gradual in some places and in others takes place across a "black front" line [16], which is a dark-gray, almost black line about 1 mm thick.

In the central zone B no trace of secondary alteration has been observed. Neogenic phases have been found in neither the vesicles nor the groundmass. All of the magnetic com-

TABLE 2. Chemical Composition of Neogenic Phases, Weight %

Oxide	1	2	3	4	5	6	7
SiO ₂	5.11	23.27	26.90	45.16	48.53	37.34	44.65
TiO ₂	1.91	0.12	0.82	—	0.56	0.12	0.02
Al ₂ O ₃	4.15	2.02	6.67	1.35	3.24	0.77	4.57
FeO	60.12	58.12	34.16	38.46	27.89	24.28	24.93
MnO	0.58	0.22	0.03	0.05	0.07	0.41	0.23
MgO	1.78	1.54	0.96	2.84	9.23	8.14	11.54
CaO	1.88	2.36	0.80	0.40	0.98	2.12	1.53
Na ₂ O	1.14	0.38	0.28	0.47	0.19	—	0.03
K ₂ O	0.65	0.40	0.97	3.25	0.21	0.05	0.12
Σ	77.42	88.43	71.59	92.00	90.90	73.23	87.62

Note. 1-4, Sample 475, medial valley of the Reykjanes Ridge; analysis by "Kamebax" microanalyzer, G. V. Karpova, Geol. Inst. Acad. of Sciences of the USSR, operator; 1) iron-silica phase from a degassing vesicle, zone A₁; 2) iron-silica phase in interstices, zone C; 3) chlorophaeite from degassing vesicle, zone C; 4) celadonite-like material from interstices near the "black front" line; 5-7) chlorophaeite composition; 5) hole 304 (northwestern Pacific Ocean), average of four analyses [12]; 6) Deccan trap, average of two analyses [18]; 7) Iceland basalts, average of three analyses [17].

ponents, including interstitial glass, are still fresh. A different picture is presented in the marginal zones A and C, where degassing vesicles are enveloped by a thin, discontinuous lining of isotropic material that is various shades of yellowish green, grading to light green and orange, in transmitted light. The surface of this lining toward the cavity has a sintery form, commonly with protrusions and gnarly knots (Fig. 3a). This material also fills fine interstices, and in marginal parts of the flow it replaces interstitial glass. In morphological setting and properties this material corresponds to the definition of "chlorophaeite" in the sense of Peacock and Fuller [18]. Along with the isotropic chlorophaeite, a weakly birefringent variety is locally encountered, and near the "black front" line material that is green in transmitted light with a strong fanlike birefringence. In the marginal parts of the flow, especially in the near-surface zone A₁, a position analogous to chlorophaeite is occupied by microscopic amorphous iron-silica phases that are bright red in transmitted light. They are located directly along the "black front" line. A gradual transition is locally found between chlorophaeite and the iron-silica phases.

Studies using the scanning electron microscope have shown that both chlorophaeite and iron-silica phases (which are differentiated by their different capacities for reflection of electrons), deposited in vesicles have irregular, complex forms resembling cauliflowers (see Fig. 3). In some vesicles the individual clots are separated from one another, while in others, especially in the lower part of the flow, they increase in quantity and form a discontinuous lining. Locally the space between individual clots is filled with porous, honey-combed material (see Fig. 3e, and f). The size of these clots varies widely.

Microprobe study of the composition of the neogenic minerals described above has shown that the iron-silica phases contain a large amount of iron and a subordinate amount of silica and other elements (Table 2). Their composition is variable but similar to that of previously known iron-silica phases from oceanic basalts [5]. Yellowish-green birefringent material near the "black front" line with a relatively high potassium content (3.42% K₂O) approaches in composition the celadonite-glaucite group, which is widely distributed in basaltoids of the ocean bottom, including the Reykjanes Ridge [5], but the high iron content prevents it from matching the crystallochemical formula for celadonite. Nevertheless, the fanlike birefringence, so characteristic of celadonite, suggests that this material has a crystalline structure applicable to the glaucite-celadonite group. The high iron content is probably related to an admixture of amorphous iron oxides. The chlorophaeite composition occupies an intermediate position between iron-silica phases and the celadonite-like material. Comparison of its composition with that of chlorophaeite from other regions (see Table 2) shows its sharp impoverishment in silica and increased content of iron and aluminum. It should be recalled that palagonite from the zone of hydrothermal discharge in the Reykjanes rift valley also differs from typical oceanic palagonites by a sharply reduced silica content and an increase in iron and aluminum.

TABLE 3. Chemical Composition of Sample 475 by Zone

Component	A ₁	A	B	C
SiO ₂	45.61	47.89	48.78	48.04
TiO ₂	0.94	0.86	0.85	0.85
Al ₂ O ₃	14.08	14.21	13.98	14.36
Fe ₂ O ₃	5.73	4.37	4.28	3.76
FeO	7.96	8.72	8.44	8.89
MnO	0.20	0.19	0.18	0.18
MgO	10.22	9.02	8.89	8.95
CaO	11.79	11.77	11.71	11.91
P ₂ O ₅	0.02	0.02	0.01	0.02
Na ₂ O	2.18	2.18	2.25	2.25
K ₂ O	0.09	0.13	0.15	0.09
H ₂ O ⁺	0.50	0.15	0.07	0.07
H ₂ O ⁻	0.43	0.30	0.31	0.42
Σ	99.75	99.81	99.90	99.79
Cr	365	260	305	340
Ni	212	177	160	162
V	330	240	282	305
Cu	83	95	107	80
Co	74	45	51	57
Pb	5	5	5	5
Ga	15	13	14	14
Ge	3	3	3	3
Mo	1.6	1.6	1.5	1.5

Note. Analyses carried out in the chemical laboratory of the Geol. Inst., Acad. of Sciences of the USSR; oxide content of rock-forming elements given in weight %; minor elements in g/ton.

The results of a study of the chemical composition of the various zones is presented in Table 3. Comparison of the compositions of the marginal zones with the central, unaltered zone (see Fig. 2) shows that the greatest divergence in content for the individual elements is in the near-surface zone A₁. The outer parts of the flow lost silica, potassium, and copper and increased in H₂O, Mg, Mn, Cr, Ni, V, and Co content. The total iron content increased insignificantly in the near-surface part of the flow, but was more oxidized. The decrease in potassium in the outer part of the flow is very interesting since an increase in this element usually takes place during alteration of basaltoids in the presence of seawater. It may be related to the actual composition of the mineralized thermal waters which caused the redistribution and removal of potassium from the outer parts of the flow.

The mode of occurrence of chlorophaeite and the iron-silica phases in the basalt flows studied clearly indicates that they were formed during free growth in open spaces, and not during solidification of residual melt. Analysis of the variation in degree of alteration of the rock and variation in content of individual rock-forming elements in different parts of the flow, and also the distribution of neogenic phases in the flow (absence in the unaltered central part and increase in amount toward the margins) attest to the effect of external solutions on the flow and the origin of neogenic phases as a result of penetration of the solutions into the flow. The location of iron-silica phases in the marginal parts of the flow, along the "black front" line, and along individual vesicle trains is apparently related to their formation in areas of active interaction in the solution-rock system. Where this interaction was less active, chlorophaeite was formed. It is probably an embryonic phase, in which the formation of both iron-silica phases and celadonite can take place during a more profound differentiation of material in the alteration process. This shows that there is a gradual transition between these phases.

The discovery of isolated manganese oxides together with these neogenic forms is confirmation of the formation of the associations described above as a result of the action of hydrothermal waters on the rock. These oxides were formed in the marginal parts of the flow in the form of patches with takyr-like surfaces (Fig. 4a) that are black in color and opaque. Distinctive manganese oxides with an egg-shaped form and a smooth, dull surface, nearly black, have also been found (Fig. 4b).

The formation of amorphous phases, corresponding to clay minerals in composition, as a result of the action of hydrothermal solution on basalts has been confirmed by numerous experimental studies (for example, [15]). The data available do not exclude the possibility of

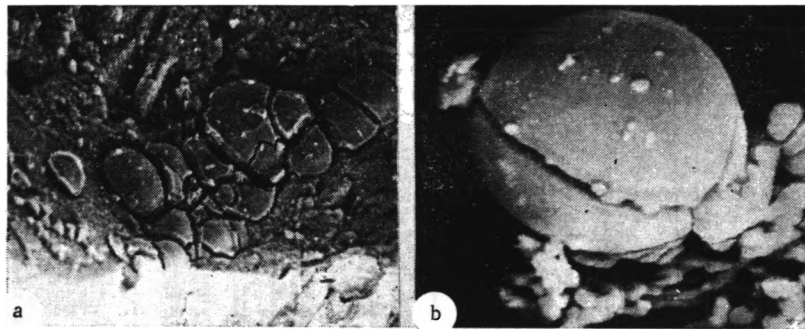


Fig. 4. Morphology of manganese oxide deposits, SEM ("Quickscam," Moscow State Univ., V. M. Grigor'ev, operator): a) $\times 600$; b) $\times 1300$.

residual melt origin of chlorophaeite under certain conditions, but indicate that this has not been found to be the case in basalts of the mid-oceanic rift valleys.

* * *

Young Holocene basalts of the Reykjanes Ridge rift valley that are away from zones of hydrothermal discharge have not undergone alteration, and Würm age basalts, only to a very minor degree. Most altered are basalts in areas of discharge of hydrothermal springs, where glassy crusts of pillow lavas have been subjected to palagonitization, while iron-silica phases, chlorophaeite, and celadonite-like material formed in basalts discharged as flows. Neogenic phases appeared as cabbage-like forms on the walls of vesicles. Their form suggests that they developed under conditions of free growth into open spaces and not as a result of consolidation of residual melt. In addition, chlorophaeite replaces interstitial glass. The outer parts of the basalt bodies were the most altered, both mineralogically and chemically. The central part remains unaltered. Alteration in the deuteric stage has not been found. All of the data taken together support the decisive role of hydrothermal activity in alteration of the mid-oceanic rift valleys. The specific composition of the neogenic phases (palagonite and chlorophaeite) depends on the actual composition of the solutions acting on the rock.

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STRUCTURES AND FORMATION FEATURES OF CARBONATE NODULES AND ENCLOSING BANDED-STRATIFIED SEDIMENTS AT THE LOWER RIDGES OF THE YENISEI

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UDC 552.12.4(571.5)

The results of a microscopic investigation of carbonate nodules and enclosing banded stratified sediments of the cryolite zone are reported. The study confirmed the late syngenetic-early diagenetic nature of these nodules.

The paper presents the results of a study of banded-stratified deposits widespread in the cryolite zone of the northern West Siberia (the lower reaches of the Yenisei) and the carbonate nodules found in them. The permafrost condition of the sediments, the high ice content, and the cryogenic structures indicate that the freezing occurred in heavily hydrated sediments on the floor of a shallowing basin [1]. This fact limits the possible time interval of nodule formation: from the time of sediment deposition until its freezing, i.e., the nodules could be formed only during syngeneses-early diagenesis. The syngenetic-early diagenetic nature of the carbonate nodules is confirmed by comparison of radiocarbon dating of the nodules and the surrounding rocks. The age of both was about the same, some 30,000 years [2].

The time of formation of the nodules, in contrast to most other cases, is clearly determined against the background of lithogenesis of sedimentary rocks. The nodule-bearing sediments themselves passed through sediment accumulation, early diagenesis, and freezing (cryogenesis), and experienced no other postdiagenetic (catagenetic or hypergenetic) alterations. Methodological and theoretical value of a detailed study of the composition and structure of these nodules and their enclosing rocks is obvious they reliably document the physicochemical and mineralogic alterations of sedimentary matter in finite water basins of the cryolite zone during syngeneses and early diagenesis.

Another aspect is important: the nodules were formed in cold-water periglacial water basin with sharp seasonal differentiation of sediment supply. Authigenic carbonate mineral formation, and especially nodule formation in such settings, have been studied little. There

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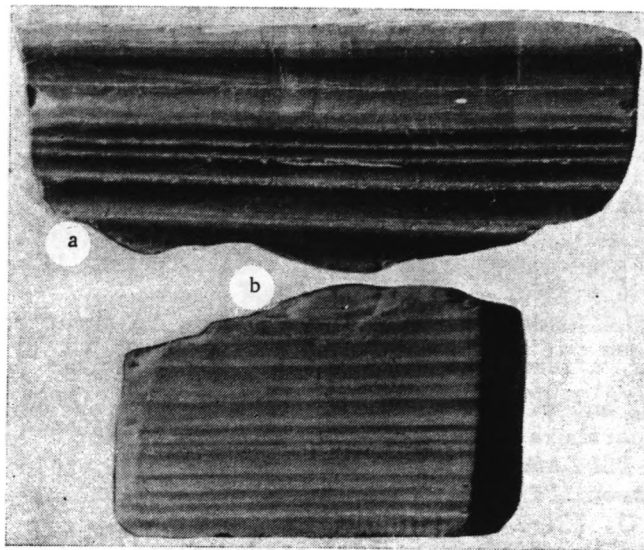


Fig. 1. Banded-stratified sediments (a - clay, b - silt).

are some data on carbonate neomorphs of a nodular type in Recent and Holocene deposits of areas with harsh continental climate in Canada and Siberia (Central Yakutia). Such units have been found in lacustrine deposits of periglacial landscapes of the Late Pleistocene in the northern North America, Europe, and Asia, to which the banded-stratified deposits studied here also belong [1]. They consist of two lithologic types: clay and slit (Fig. 1).

The rhythmic banded stratification in the clays is finer, most of the bands are 2-5 mm thick, and more distinct; in siltstone the bands are thinner (from 0.5 to 10 cm), and less manifest. Some of the bands are typical cyclothem with a succession of more or less sandy or clayey interlayers. The boundaries between interlayers are gradual within bands, and sharp, sometimes wavy, between the bands, with grains of coarser sand found at the base of the sand layer which begins the next band - the cyclothem.

The accumulation of banded-stratified sediments of predominantly siltic or clayey composition took place mainly in freshwater basins, as confirmed by microfauna (ostracods) and microflora (diatoms). Toward the mouth of the Yenisei the sedimentation setting gave way to brackish or even low-salt seawater environments, confirmed by the finds in light siltstone layers of shells of *Portlandia arctica* (Gray) var. *aestuariorum*, which is an arctic marine mollusk [3] capable of surviving in substantially desalted habitats and found in estuaries of northern rivers, in particular, in the present-day Yenisei Bay.

For microscopic study we took the most indicative lithologic type of banded-stratified sediments - clays; these in turn are divided into two varieties. Most clays are fine stratified (with bands of 2-4 mm) varieties, with predominant clay interlayers in some of the bands and subordinate role of fine-sand-silt layers. At the top and bottom of the profile of banded-stratified strata, the structure is different: the bands increase in thickness to 10 mm, with fine sand and silt component becoming predominant; this is the second variety of banded clays. The two varieties of banded-stratified clays are characterized below.

The clay interlayers in the bands account for about two-thirds of the thickness of fine stratified clays. Within each, three to four inconsistent microlayers up to 0.3 mm thick can be traced, which sometimes contain heightened amounts of isotropic organic matter with scattered globular pyrite. The clay is brownish, with an interference in gray-yellow tones with perfect orientation and simultaneous extinction of the entire layer. The layers contain individual angular quartz grains of 0.001 mm, fragments of vegetable tissue with cellular structure, 2-3 mm across, disseminated globular pyrite, and apparently secondary brownish segregates of iron oxides.

Fine-sand-silt (light) interlayers in the band consist of angular and semirounded grains of quartz, feldspar, plagioclase, and monoclinic pyroxene. Minor amounts of chlorite, muscovite, and ore minerals are present. There are also single inclusions of larger grains of basaltic porphyrite, dolerite, sandstone, and marble. Amorphous iron oxide clots and rounded

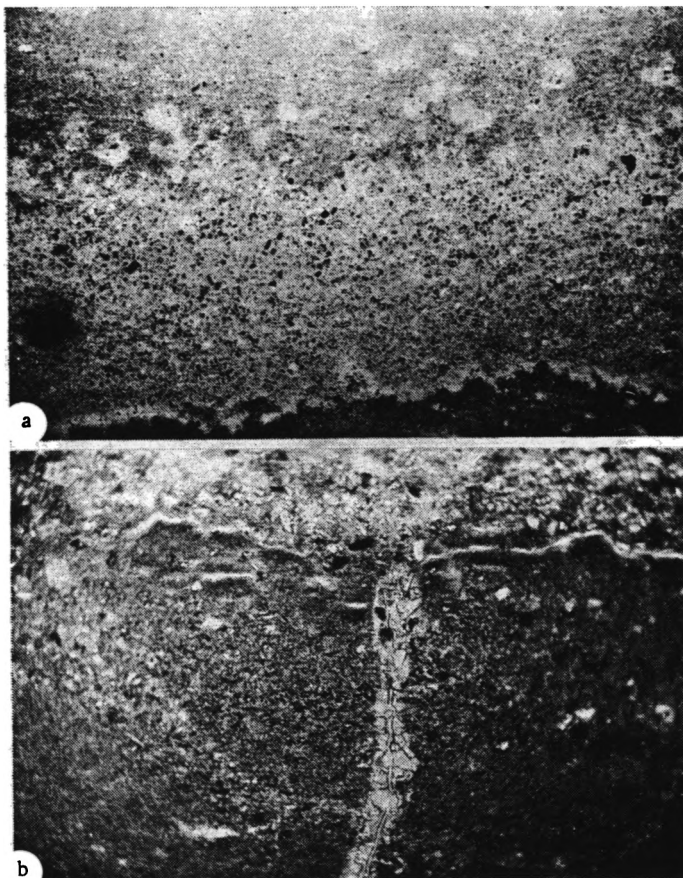


Fig. 2. Types of contacts between bands (cyclothem) and within bands: a) two uneven contacts with plastic intrusion microtextures ("loads"). A distinct boundary between adjacent bands seen at the bottom: silt-sand (light) layer of one band, and slit-clay (dark) layer of subjacent band; top: indistinct boundary between lower (more sandy) layer within the band and upper (more clayey) layer. Spotty fragments of sandy band layer at the base of overlying clay layer are seen. Magnification $\times 90$, crossed nicols b) diagenetic compaction cracks along horizontal contact of bands; larger vertical cracks sink downwards from them. Both crack systems filled with authigenic carbonate. Magnification $\times 90$, crossed nicols.

and bean-shaped microsegregates of organic matter are also typical. The presence of evenly distributed clay rounded pellets in the fine-sand-silt mass (up to 5%) is remarkable. At the contact of the sandy interlayers with their subjacent clay interlayers, microtextures of intrusion of one layer into another can be seen, as well as accumulations of clay pellets; these are signs that as sand-silt material accumulated, the underlying clay layer was roiled, coagulated, and precipitated together with the clastic particles. The boundary of the sand and clay interlayers within a band is gradual and uneven, with "eddies" due to plastic microintrusions of sand material into the clay (Fig. 2a). Fragments of sand interlayers are often broken away from them, and the boundary then acquires a ramified pattern resembling oak leaves. Diapir-like intrusions of clay interlayers into overlying sand layers do not violate the generally distinct boundary between the cyclothem bands; no separated fragments are observed here.

Plastic deformations at the discontinuity boundaries of bands and, inside them, lithologically different interlayers, certainly occurred during sedimentation in moist loose grounds: these are as it were "load" microtextures, often formed in bottom sediments, and characterized by a larger size. Here they are seen in a microscopic scale, confirming the basic similarities of the physical diagenetic processes in basin sediments on the macro- and microlevels.

The banded stratified clays of the second type are characterized by the prevalence of silt-sand layers, with the clay being subordinate. In the former, clastics consist mainly

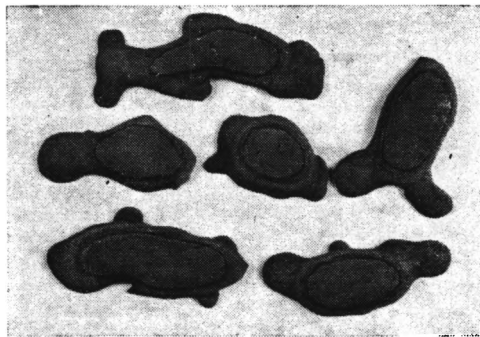


Fig. 3. Flat valve-like figure-shaped carbonate nodules from banded-stratified clays, lower reaches of Yenisei. Reduction 2 $\times$.

of a fine sand fraction with a heightened pyroxene content (up to 15%). There is also more terrigenous matter in clay interlayers. Burrows of a rounded wormlike or irregular shape, depending on the cross sections, are abundant. They are perfectly visible against the background of a finely dispersed clay material, because they are filled with a coarser matter. Diagenetic compaction cracks and microrupture faults are also observed in clay layers. A typical picture exhibits consistent horizontal cracks along the bedding surfaces between the bands and the base of the sand interlayer, with vertical cracks proceeding from them downward (see Fig. 2b). Carbonates migrated along cracks with interstitial solutions, and then precipitated. Carbonate segregates are typically linear, steplike, less often droplike.

Comparisons show that plastic deformations of virtually liquid sediment, without disrupting the continuity of layers, are typical for finely stratified clays with prevalence of clay in the bands. In the clays where the layers are thicker and the differentiation of material into coarser and finer, fractions is sharper, cracks and microruptures healed with carbonate were formed in the course of diagenetic compaction. Pyrite globules were probably formed at the early stages of diagenesis, at sites of organic accumulation.

Nodules are found both in banded-stratified clays and in siltstones. These are compact units consisting of the material of the enclosing rock, cemented by finely stratified carbonate. Nodules are mostly flattened (Fig. 3) and have a definitive shape of a disk, a button, a blade, less often a sphere; when nodules grow together, their shape becomes more convoluted, with beadlike and grapelike structures, etc. Flattened nodules are 2-5 mm thick and 5-50 mm across; spherical nodules are usually 5-10 mm across. The nodules are of a light or off-gray color; the broken surface is even. Inside a nodule, banded stratification is clearly seen with alternation of more clayey and more sandy interlayers; in the clay the layers become thinner toward the edge of the nodules, while in the silt they, as it were, pass through the edge without changing their thickness. The sand-silt interlayers in nodules have the higher carbonate content, and react more actively with 10% HCl.

The mineral composition of nodule carbonates is calcite, with an admixture of acicular aragonite. Carbonates account for, from 22.5 to 58.5% of the nodular matter [1]. In the enclosing banded-stratified sediments the amount of carbonates is highest in sandy siltstone and lowest in clays; in some of the bands it is largest (1.8%) in sand-silt interlayers, and lowest (0.6%) in clay layers. In other words, carbonate contents are sharply differentiated according to the lithology of the sediment. Most nodules have a high manganese content, with MnO amounting to 1.8-2.6%, as against 0.1% in the country rocks. The carbonate content of the the silt interlayers is probably associated with the active seepage of CO₂ through them and precipitation of CaCO₃ from interstitial solution. CO₂ leaked also through diagenetic compaction cracks, which were healed by carbonates falling out of the solution.

The microstructure of the nodules is largely predetermined by the structure and textural features of the enclosing rocks, and the differences in the composition, grain size, and distribution of clastic matter. The nodules from the banded-stratified siltstone exhibit distinct alternation of layers with coarser and finer clastics; the clay and organic impurities are also distributed layer-by-layer. Elongated quartz grains are oriented, with the major axis strictly along the band discontinuity boundaries. In clay interlayers within the nodules, the material has a random structure and is carbonatized evenly. The clastic component

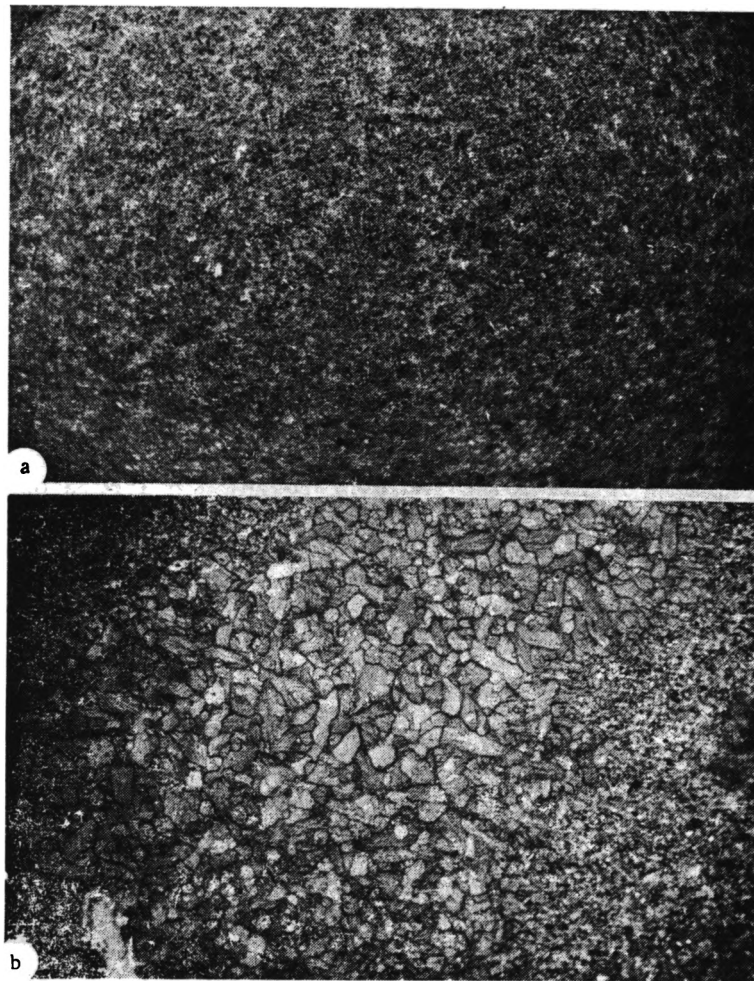


Fig. 4. Various types of internal structure of nodules: a) floccular oriented structure of nodules from banded-stratified clay: light-fine disseminated carbonate cement with white spots (resulting from carbonate replacing larger clastic grains). Magnification 90x, crossed nicols; b) texture of recrystallization areas in carbonate cement: carbonate grains are seen to grow in size from the perimeter toward the center. Magnification 90x, crossed nicols.

consists of quartz, feldspar, plagioclase, monoclinic pyroxene, chlorite, ore minerals, and basaltic porphyrite fragments. Quartz is clearly predominant. Finally, dispersed carbonate matter binds together the clastic grains; the cement is interstitial. The carbonate is microgranular (<0.05 mm), and cryptocrystalline; collectively with clay material it forms a mass with a characteristic golden-rainbow interference. It corrodes the grains of all minerals, forming characteristic erosive shapes at edges.

Stratification is less pronounced in nodules from banded clays with predominant clay component. The nodules have either striated or unstratified, oriented or unoriented structure.

The oriented striated structure in nodules is formed by carbonate grain aggregates occurring as parallel strings and vaguely contoured strips. The oriented floccular structure of nodules was apparently produced by complete carbonate substitution of clastic grains, as indicated by neomorphous carbonate spots amid clay-carbonate mass (Fig. 4a). The microgranular clay mass cemented with carbonate in nodules of an unoriented structure contains clay micropellets and also angular and semirounded grains of quartz, feldspar, plagioclase, volcanic glass, and single biotite laths. The structure of the nodule material is lumpy; the carbonate cement is crystallized unevenly, and forms rounded or oval segregates up to 0.5 mm, with microgranular texture. The carbonate grains in them are of an irregular elongate form, "sticking" to one another, and exhibiting golden interference colors. Carbonatization areas of this texture are confined to accumulations of clay pellets, plant remains; sometimes they envelope quartz grains.

All three types of nodules from banded clays bear signs of a deeper alteration of the initial sedimentary material, as compared with the banded-stratified siltstones; this alteration sometimes results in total substitution of neomorphous carbonate for the clastic grains. Recrystallization textures of carbonate cement are also observed in them: sheaflike grains 0.5 mm. They fill irregular segments in clay-carbonate mass, and form up to 30% of the nodule. The boundaries between recrystallization portions, and the main clay-carbonate ground-mass are sharp; at the site of recrystallization segments, the boundary is lined with smaller carbonate grains oriented with the major axis perpendicular to the boundary. Toward the center of the recrystallization segments, carbonate grains become larger (see Fig. 4b). Clastic grains are either absent in recrystallization areas or fully replaced with carbonate, indicated by the regular rounded shape of carbonate segregates.

The data on microstructure and composition of nodules and enclosing rocks suggest some conclusions as to their formation conditions. Nodules began to grow in loose moist sediment; the process involved the capture of clastic material by the carbonate nodule formant and the filling of interstitial space. The diagenetic compaction cracks and disruption faults in enclosing banded clays, and the absence of these signs inside nodules, show that the latter were formed before the compaction of the moist sediment began. In liquid ooze, processes associated with uneven loading and convection at the interfaces of lithologically heterogeneous sediments took place. Subsequent compaction and dehydration involved the formation of microcracks in lithologically distinct varieties of banded clays. Compaction also occurred in the nodules (although less intensely), as shown by reduced thickness and even wedging-out of the interlayers toward the edges of the nodules. This fact also indicates a radially concentric growth of nodules from the center to the perimeter with subsequent cementing of the terrigenous sediments that were gradually compacted. In addition, the clay ooze experienced profound chemical and mineralogic alteration of the terrigenous material during the course of nodule formation, and some of the mineral grains and clastics were replaced by carbonate. Carbonatization continued even after substantial dehydration of the sediment, leading to diagenetic compaction of cracks subsequently healed with carbonate.

Sand-silt sediments are less subject to setting after dehydration and compaction. Inside the nodules from the sand-silt sediments, primary sedimentary structure is therefore better visible; some of the layers pass through the longitudinal cross section of nodules with out changing in thickness. Apparently, carbonates were precipitated from interstitial solutions in conjunction with CO₂ leakage, in a process that was basically sedimentary and was not associated with any profound or even noticeable alteration of the terrigenous matter inside the nodule.

The study of the microstructure of carbonate nodules confirmed reliably that they are of a late syngenetic-early diagenetic nature [1], and determined the features of the lithogenesis of basin sediments at the early stages of the process. The basic possibility of authigenic carbonate formation in cold-water freezing-bottom settings of cryolite zones has also been confirmed, given a favorable combination of natural factors.

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A new commercial deposit of dolomites of a chemogenic-metasomatic genesis is described. Dolomites are classified according to a set of features, with secondary-epigenetic entities formed from high-magnesium low-temperature solutions as a result of hard limestones experiencing metagenesis and tectonic reworking.

In 1983-1984 the authors studied Tkvarcheli deposit of dolomites in Abkhazia. These studies produced data which have drastically changed the notion of the composition, the shape of the ore body, the tectonics, and the genesis of this deposit, as determined by previous geologic exploration.

Detailed reconnaissance was conducted in this deposit in 1967-1968 and 1976-1977, with additional exploration in 1981-1982. The deposit is used as the source of raw materials for metallurgical dolomite used at Rustavi metalworks. The official estimate of dolomite reserves is 41 million metric tons, including 20 million metric tons complying with the standard TU-14-8-232-77, according to the engineering studies [7]. The dolomite of the commercial bed has a low content of silica (0.02-1.29%), aluminum (0.01-0.70%), and low contents of alkalies (0.04-0.08%), and sesquioxides and sulfur. MgO content varies from 11.45 to 19.0%, sometimes attaining 21.85%, in conformity with theoretic estimates. The importance of this deposit is emphasized by the fact that for years to come it will be the main source of converted dolomites for metalworks in the European USSR.

The deposit is situated on the watershed of Aistra ridge, and stretches from northwest to the southeast. It is located at the juncture of two geotectonic structures - the Georgian mass in the south with a folded cover, and the foldbelt of the noted southern slope of the Greater Caucasus in the north, with its widespread overthrust structures. The boundary between the two structures passes along the tectonic contact, tracing the lateral overthrust separating the Jurassic and the Cretaceous, and determining the complex tectonic setting of the deposit and the specifics of the dolomite genesis.

The geological structure of the deposit is formed of Jurassic, Cretaceous, and Quaternary age sequences. The continental coal-bearing units of the Jurassic are to the northeast of the deposit; they dip gently to the southwest, and have a tectonic contact with the lower Cretaceous strata (Fig. 1). The lower Cretaceous products of sedimentation, stretching as a broad band from the northwest to the southeast, exhibit a steep, almost vertical, southwest dip.

At the base of the dolomite body are Valanginian and Hauterivian limestones with tectonic breccia at the contact with Jurassic. Tectonic breccia gives way to dolomites and stratified sandy limestone formed of fine-grained calcitic mass with clay matter. Silicic diatom remains, 0.08-0.12 mm across, are discernible in the fine-grained limestone, with rare pointlike inclusions of ore minerals and thin calcite veinlets. The Valanginian-Hauterivian attains 100 m in thickness. At the roof of the paybed, Barremian limestones occur. These rocks are recrystallized, have an organogenic-clastic texture, and consist of carbonate remains of organisms and small, slightly rounded fragments of pelitomorphous limestone cemented with small crystalline calcite. In contrast to the subjacent limestone bed, this layer contains no quartz sand grains. The Barremian is 400 m thick. Up the profile, the Barremian limestone is succeeded without interruption by limestones and carbonaceous sandstones of the Aptian and other sediments (see Fig. 1). The geologic mapping of the operational quarry has determined that dolomites of the paybed are epigenetic, and were formed after limestones of both Valanginian-Hauterivian and Barremian stages.

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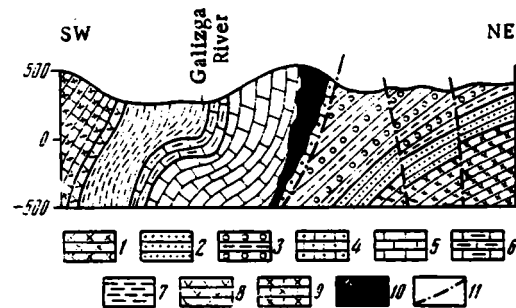


Fig. 1. Geological profile of the area of Tkvarcheli dolomite deposit (after Narimanidze, supplemented by authors). Jurassic system. Middle series: 1) Bajocian (porphyrite, tuff-breccia, tuff-sandstone); 2) Bathonian coal-bearing suite (argillite, siltstone, sandstone with bituminous coal seams). Upper series: 3) Kimmeridgian variegated suite (conglomerate sandstone and clay with gypsum layers). Cretaceous system. Lower series: 4) Valanginian and Hauterivian stages undivided (sandy limestone); 5) Barremian stage (coarsely stratified limestone); 6) Aptian (sandy limestone and marlstone); 7) Albian (marl and clay). Upper series: 8) Cenomanian (glauconitic sandstone, marl, and limestone); 9) Turonian and Danian stages undivided (limestone); 10) dolomite body; 11) lines of tectonic dislocation.

Investigations have been performed with conventional methods described in publications [5, 16-18, 20, 29, 30, 41, 42], to study the genesis of dolomites of this deposit. There have been various genetic classifications of dolomites; we believe that the most exhaustive classification was suggested by Rukhin [30], who distinguished: primary-sedimentary dolomites (corresponding to the primary sedimentational rocks, after Strakhov [31] and protogenic, after Vishnyakov [10], and chemogenic, after Teodorovich [35, 36]), syngenetic and diagenetic dolomites formed as a result of ooze alteration; and secondary (epigenetic) dolomites created from already hard limestones affected by various solutions. The possibility of epigenetic formation of dolomites remained questionable until the studies by Kholodov et al. [43, 44], who demonstrated convincingly the possibility of dolomitization from brines and circulating underground waters, which dissolve sedimentary-diagenetic dolomites in the supply area and form epigenetic dolomites in the discharge area.

The stratal occurrence and the massive body are considered the distinctive features differentiating the primary and sedimentary origin of dolomites [10, 28, 31, 35]. Stratal occurrence implies the existence of sedimentary roof and foot. Detailed investigations have determined that within the deposit, the body of the mineral is represented by a bedlike vertical lens, varying the explored area from 15 to 245 m in width. Along the course, the lens has been traced by mine workings over 1.2 km. Exploratory surveys have determined that the dolomites, while wedging out periodically, stretch far to the northwest. The dolomite deposit is exposed by erosion to a height of 500 m. The contacts of dolomites and limestones were determined in the course of exploration by a rapid chemical analysis; it was assumed that the limestones at the roof and the foot of the ore body were not different macroscopically from dolomites. The contours of pay deposits of dolomites and the interlayers of substandard carbonate rocks within the commercial bed were determined by a similar procedure. The internal structure of the paybed was simple. In the middle portion, a zone of converted dolomite was identified, while the peripheral areas were zones composed of layers of metallurgical varieties (Fig. 2).

The geological mapping in the open-cast mine determined that the body of the commercial deposit did not have a stratal structure; in addition, the sedimentation roof and foot exhibited no zonality in the occurrence of converter dolomites; there was no bed of metallurgical dolomites. The transitions between dolomites and limestones were sharp; they occurred over a spacing of 3-5 cm, with intense branching of limestones transformed into dolomites. The narrow zone at the contact between dolomites and unaltered rocks is known as the dolomitization front [48], which is an indicator of an epigenetic genesis of dolomite [19, 26].

The transition contours between dolomites and limestones are meandering, and do not inherit the stratification. They are especially variable near zones of intense cracking and tectonic dislocations, and are compounded by postmineralization tectonics and dedolomitization

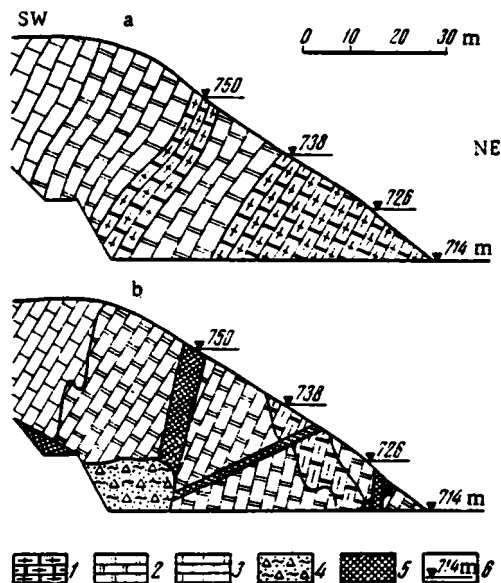


Fig. 2. Geological profiles of the commercial beds according to reconnaissance (a) and based on subsequent analysis (b): 1) dolomites suitable for converter refractory materials; 2) metallurgical dolomites; 3) limestone; 4) karst filling (clay-cemented limestone fragments); 5) crushing zones; 6) worked horizons.

and karsting. The analysis of the data indicates that the dolomite-limestone contact is not a bedding plane, but a wavy surface with different bends at different mining horizons, and horizontal shifts of 10-30 m. The general course of the ore body is southwestern, with dip angles close to 80° (Fig. 2). The internal structure of the deposit is also more involved than was assumed after geological exploration. Documents and open-cast mine tests have identified converter and metallurgical dolomite varieties, and limestones of dedolomitization and filling karst cavities. In the upper horizons (750 and 730 m), the commercial deposit consists mainly of metallurgical dolomites, with rare small bodies of converter dolomites. In the horizon of 726 m, seven converter bodies appear amid metallurgical dolomites. Their horizontal cross sections vary in shape from nearly round, 5-40 m in diameter, to elongate ellipsoid and lenticular shapes 2-8 m wide and 6-40 m long. Further down, in the 714 m horizon, are eight bodies of converter dolomites, with increasing dimensions up to 40×60 m.

The contacts between converter and metallurgical dolomites pass mainly along the line of tectonic faults and the associated crushing zones. The disruptions break the body of the deposit into blocks ranging from 15×15 to 35×35 m. The analysis indicated an increasing quantity of converter dolomites from the upper horizon (750 m) to the lower horizon (714 m), from 12 to 50%, respectively. Despite the increase of the converter dolomite amount in the lower horizon, these dolomites do not form a continuous deposit, and are concentrated in separate bodies.

The contours of the deposit and the technological types of dolomites exhibit a selective and peculiar pattern in an absence of the stratal formation, suggesting an epigenetic origin of these dolomites.

The dolomite bed in the deposit does not occupy any distinct stratigraphic position. Both limestones of the roof belonging to the Barremian stage and the limestone of the foot, dating from Valanginian and Hauterivian, have been dolomitized. The distribution curves of sand grain sizes always convey genetic information [30, 45]. The dolomites and limestones contain terrigenous impurities; the distribution curves of sesquioxides and silica in carbonate rocks of the deposits were compared in order to identify the limestones that experienced dolomitization. All the curves of silica distribution (Fig. 3) are asymmetrical, with the peaks shifted to the left. The silica distribution curve in Valanginian-Hauterivian limestones is a multipeak curve with five maxima at points with SiO_2 content equal to 0.5, 1.2, 2.0, 2.7, 3.4%. It differs from the Barremian limestone curve, which has two peaks. In contrast, in dolomite the silica distribution curve is the resulting plot that occupies an intermediate position between the above two plots. The distribution of sesquioxides is similar. The Valanginian-Hauterivian limestone curve also has five peaks at 0.25, 0.45, 0.75, 0.95, 1.15% R_2O_3 . The

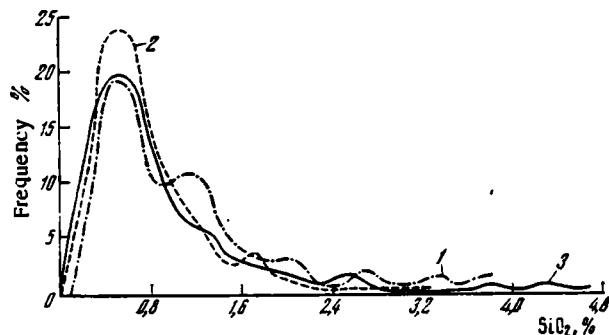


Fig. 3. Silica distribution in carbonate rocks: 1) Valanginian and Hauterivian limestones (170 analyses); 2) Barremian limestone (575 analyses); 3) dolomite (764 analyses).

rhythmic recurrence of peaks after every 0.20% apparently represents the cyclic accumulation of the terrigenous component. The curve for Barremian limestones has two peaks. Similar to silica, the sesquioxide distribution curve in dolomites is the resultant of the preceding two. For example, the modal content of R_2O_3 in the former is 0.266%, in the latter - 0.2%, and in dolomite is the mean of the two (0.233%).

Differentiation of structural dolomite classes also provides genetic information [28, 34]. Pelitomorphic dolomites with grains smaller than 0.001 mm exist as biochemogenic and evaporitic rocks; small-crystalline grains measuring a few one-hundredths of a millimeter were produced by precipitation of high-magnesium carbonate ooze; fine-crystalline dolomite with crystals of several one-tenths of a millimeter are characteristic for diagenetic, less frequently catagenetic limestone replacements; and phanero-crystalline dolomites, one-tenth of a millimeter and larger, are formed almost exclusively after dense rocks.

Dolomites in Tkvarcheli deposit are off-white-gray, light-gray, often pink-white, spotty, highly porous, with sugarlike phanero-crystalline texture. The high porosity of the dolomites was noted in geological documents describing the cores from boreholes, shafts, quarry walls, and microscopic studies of polished sections. Microscopic investigations of grain sizes sizes determined three varieties of dolomites in this deposit: fine grained, with grains of 0.05-0.1 mm; medium grained, 0.2-0.4 mm; and coarse grained, 0.45-0.6 mm. Medium grained varieties are predominant, and account for some 50% of the commercial bed, followed by coarse grained (30%), and minor quantities of small grained dolomites (20%). The dolomite grain sizes often vary largely over short distances, both to the strike, to the dip, and across the deposit.

Polished section studies have identified mostly mosaic textures in dolomites, which often inherit "shadows" of skeletal remains of organisms, sculptures, and structural patterns of limestones. They consist of densely packed rhombohedra, sometimes with distinct zonality and abundant accumulations of coarse grained transparent calcite. Cavities up to 0.5 mm often occur between rhombohedra. The phanero-crystalline appearance, the grain size, and the presence of skeletal tissue remains of the limestones suggest that these dolomites developed as a replacement of already hardened rocks.

The mosaic texture, the sugarlike sparkling broken surfaces, high porosity, absence of selectivity in dolomitization, and the presence of dolomitized fields with meandering contours and loss of facies difference and sedimentary boundaries are characteristic of secondary sedimentary dolomites [27, 28]. The segregation of crystals in the form of a mosaic suggests that the replacement occurred in previously formed rock, under the impact of external factors. Large crystal sizes combined with zonality represent both the long duration and unfavorable conditions of growth [35].

Among the dolomite structures, investigators distinguish primarily sedimentary structures produced by accumulation of magnesian-carbonate sediments and associated with replacement processes. Botvinkina [6] notes that the typical structure of chemogenic dolomites is a thin parallel-horizontal stratification with layers of 1-2 mm, quite consistent to the strike. No fine stratification has been observed in dolomites of this deposit, although a relict, slightly blurred stratification inherited from limestones is sometimes noted. Generally, they have a massive appearance because of the cementing of cracks and cavities in epigenetic dolomites by dolomitic material, which has a high degree of crystallization and relatively large grains. By these features, these dolomites cannot be classified as sedimentary.

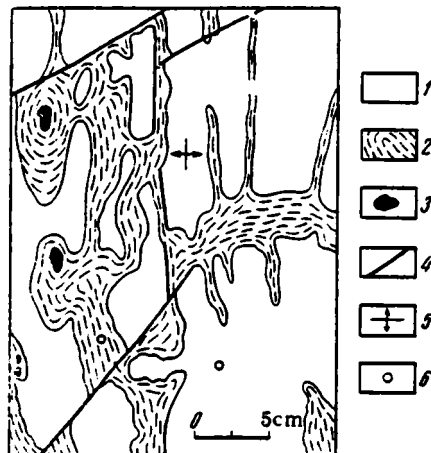


Fig. 4. Dolomite sketches: 1) small-crystal white replacement dolomite formed after limestone; 2) light pink, slightly grayish large crystal chemogenic dolomite; 3) cavernous channels; 4) cracks; 5) direction of relict stratification; 6) specimen collection sites.

The main structural feature of these dolomites is their spottiness, not described in previous geological explorations. A detailed analysis of the spots shows (Fig. 4) that the groundmass of dolomites has a large-block clastic structure with fragments of 0.3-0.8 m, exhibiting white color and sugarlike appearance; microporous rocks are formed of rhombohedral dolomite crystals measuring 0.3 mm, with a distinct zonality (alternation of dark and light zones parallel to faces). These blocks are also cemented with a dolomite rock with a light pink, slightly grayish pigmentation. Under the microscope the cement of this rock exhibits distinct large rhombohedral crystals up to 6 mm, merging into a continuous mosaic. The cement is microporous, and contains rare inclusions of ore minerals. The dolomite cement fills the cracks, which are parallel or perpendicular to the layers (see Fig. 4). To an extent, the sharp angles of the fragments being cemented are smoothed by this process. At some nodes at intersections of the cemented cracks are caverns - round channels from 3 mm to 3 cm in diameter, with relatively smooth inner surfaces covered by a carbonate crustlet, usually consisting of several thin layers. Inside the channels, brushlike growths of small transparent calcite crystals are sometimes seen. The transition zones between these two dolomite varieties which form the deposit has been studied; the study shows that they are distinct, and can be traced over stretches of 2-3 mm. This seems to indicate an interpenetrational or partial etching of clastic dolomite by the cementing dolomite. The relict stratification is observed only in dolomites of the first variety, while cementing dolomites have a massive structure, although macroscopically indistinct flow structures are also seen in them. This complex pattern of the dolomite bed indicates that the rocks were formed by concentrated high-magnesium solutions acting on limestones.

In order to determine the forms in which magnesium oxide occurs in carbonate rocks of this deposit, five specimens with MgO content of 2.4-19% were investigated by x-ray structural analysis. The resulting diffraction patterns (Fig. 5) contain dolomite and calcite reflections [22]. Specimen 1 in diffractograms exhibits only dolomite reflections. Based on the data of chemical analysis, the formula of the mineral has been calculated: $\text{Ca}_{0.53}\text{Mg}_{0.47}\text{CO}_3$. This mineral corresponds to protodolomite, or a dolomite-like rhombohedral carbonate with a fully-ordered structure of the crystalline lattice and a tendency for being enriched in isomorphous impurity of CaCO_3 . The protodolomite, which has ordered cation positions, is not identical with pseudodolomites, where the cation positions are disorderly [47]. In the deposit, mean dolomite content in the commercial bed was 84.36%, also confirming the presence of protodolomite. Experiments and in situ observations determined [14] that protodolomite is an intermediate phase of hydrothermal dolomite synthesis and of dolomitization at low temperatures.

The diffractogram of specimen 2 with MgO 16.5% and CaO 34.5% displays reflections 3.035 and 1.875 Å of a very low intensity (<2 points) typical of calcite, while for the first plane, the normal intensity of calcite is 10 points, and for the second - 8 points. This suggests that most of the specimen consists of protodolomite, with a small calcite admixture. Diffractograms of specimens 4 and 5, consisting of limestone with magnesium oxide contents of 2.4

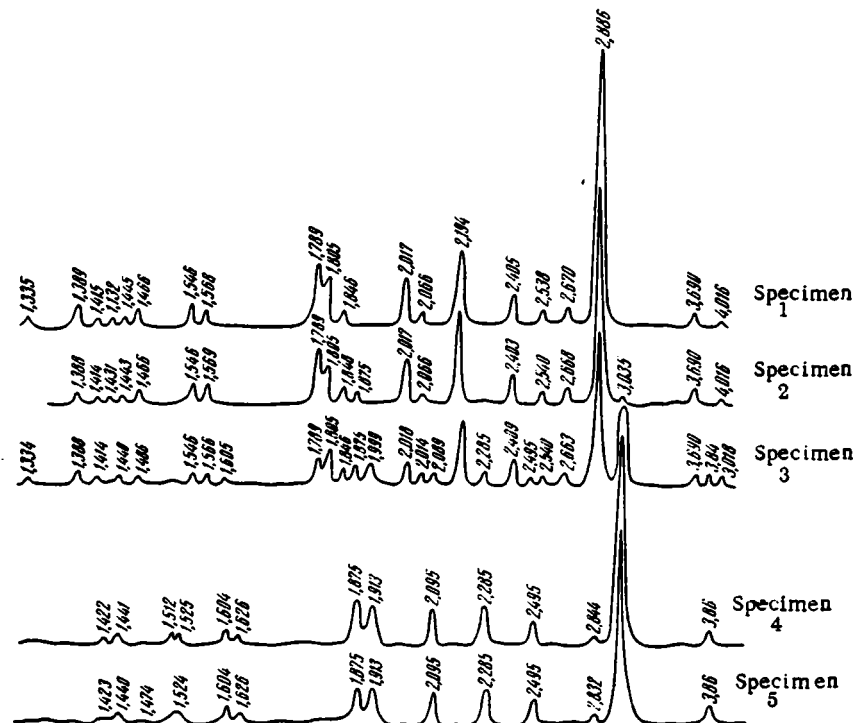


Fig. 5. Diffractograms of carbonate rocks. Specimen 1: protodolomite; specimen 2: dolomite; specimen 3: de-dolomitization limestone; specimens 4 and 5: magnesian calcite.

and 6.2%, respectively, display reflections which are unique to calcite. Probably, magnesium makes part of the composition of a calcium mineral - magnesian calcite, which can include up to 15 mol. % of calcium carbonate in its lattice [12]. The chemical formulas of magnesian calcite are $\text{Ca}_{0.94}\text{Mg}_{0.06}\text{CO}_3$ and $\text{Ca}_{0.85}\text{Mg}_{0.15}\text{CO}_3$, respectively.

The relationship between dolomite content and insoluble residue depends on the genetic type of the dolomite. It has been shown [14, 25, 28, 46, 49] that this correlation is positive in rocks with sedimentary or sedimentary-diagenetic dolomite, while in rocks with replacement dolomites it is uncertain. In order to determine the presence of a correlation between MgO , CaO , SiO_2 and R_2O_3 in carbonate rocks of the deposit, cross-correlation coefficients were computed. The resulting matrix (Table 1) reveals no correlation between MgO and sesquioxides and silica in the dolomites. The absence of such correlation confirms that these are replacement dolomites. There is an inverse relationship between MgO and CaO , with correlation coefficients for dolomites -0.83 , and for limestone -0.88 . The high negative correlation between CaO and MgO is to be expected because these components constitute dolomite mineral, while an equally significant correlation in enclosing limestones confirms the x-ray structural analysis showing that limestones are composed of magnesian calcite. The limestones have a correlation between sesquioxides and silica equal to 0.78 , indicating that clays are the main impurity. In dolomites this correlation is greatly subdued.

The diagram describing the relationship between dolomite content and silica content in carbonate rocks show that, at abnormally high silica contents, dolomite contents are higher in three cases out of ten. A review of specimens with more than 4% silica determined that they were all collected within zones of crushing and intensive cracking of the commercial bed.

The strontium content in limestones, based on quasiquantitative spectral analysis attains in some specimens 300 g/ton (average 70.8 g/ton). In dolomites strontium is not higher than 200 g/ton (mean 11.7 g/ton). Na_2O content, according to chemical analysis in the enclosing limestone, is 0.24% (mean 0.11%), while in dolomite it is not higher than 0.08% (mean 0.06%), i.e., is virtually within the sensitivity of the method. The sharp drop of sodium and strontium contents in dolomites, as compared with limestones, is a typical sign of superimposed dolomitization, and an additional confirmation of their epigenetic origin [28].

TABLE 1. Cross Correlation Matrix of Principal Chemical Components in Carbonate Rocks

Component	Correlation coefficient				Statistical indicators		
	MgO	CaO	SiO ₂	R ₂ O ₃	mean $\bar{X}$	standard S	variation coeff. V
MgO	1	-0.88	-0.14	-0.12	2.37	2.40	101.45
CaO	-0.83	1	-0.04	0.02	52.12	2.98	5.73
SiO ₂	0.04	-0.18	1	0.78	1.12	0.63	55.14
R ₂ O ₃	0.06	-0.14	0.37	1	0.38	0.27	38.64
Mean $\bar{X}$	19.31	32.59	1.03	0.46			
Standard S	1.27	1.55	0.49	0.29			
Variation coeff. V	6.81	4.67	44.93	59.71			

The different geochemical histories of strontium and barium in hypergenetic zone can be used to separate the two elements and use the strontium-to-barium ratio to distinguish freshwater and seawater settings [1]. The ratio will be smaller than 1 in freshwater basins, and larger than 1 in seawater basins. This ratio for Tkvarcheli limestones is 6.2, suggesting a normal marine setting, while for dolomites it is 0.6, which would be typical for freshwater deposits, and does not correspond to conditions where carbonate facies are formed.

A marine origin of the carbonate material of dolomites is indicated also by the chemical composition and mineralogy of clays filling the cracks in karsting zones of dolomites. It has been established [1] that the chemical composition of finely dispersed matter of different rocks, including carbonates, does not experience any major change during catagenesis, metamorphism, and probably initial metamorphism. The clays were studied by a set of techniques, including x-ray structural and chemical investigations. The basal reflections in diffractograms of 14.6-14.8 Å in natural specimens, and 17.8 Å in glycerine-saturated specimens, determine the clays as substantially montmorillonitic [21] with admixtures of calcite, beidellite, and saponite. Their contents are %: SiO₂ 33.29-41.96; Al₂O₃ 15.36-21.80; TiO₂ 0.52-0.82; Fe₂O₃ 4.05-8.37; FeO 0.24-0.83; MnO 0.02-0.04; CaO 4.86-17.95; MgO 2.57-2.94; K₂O 0.41-0.75; Na₂O 0.04-0.07; P₂O₅ 0.07-0.20; S 0.01; annealing loss 17.70-25.88. By their chemical composition, these clays belong to alkaline-earth montmorillonite, which is indicative of normal marine sedimentation setting of carbonate rocks [33]. Montmorillonite is formed in a marine environment in a humid climate at moderate depths, as a result of replacement of micas, hydromicas, and other minerals affected by alkaline solutions [8]. The formation of chemogenic dolomites involves a synthesis of clay minerals represented by palygorskite and sepiolite, and occurs in an alkaline environment rich in cations (especially magnesium) in arid and semiarid climates of marine and saltwater (lakes and lagoons) basins.

Another convincing proof of a replacement genesis of these dolomites [38] is the presence of organic remains composed of dolomite, but originally segregated as high-magnesium calcite, because there are no dolomitic organism remains. Dolomitic replacement of the remains of microorganisms composed of pelitomorphous calcite is clearly registered in some polished sections under the microscope. For example, in a specimen collected at 249 m from the mouth of the shaft at dolomite-limestone contact, Bagrimova described a variety of limestone-dolomite transition, which is rather rare for this deposit: a dolomitized limestone with porphyroid texture built of large aggregates of dolomite rhombohedra, with distinct fragments of pelitomorphous calcite in the matrix and carbonate organism remains in the shape of oval plates and rods, apparently coccolithophores [40]. In some polished sections dolomite is seen to replace remains of microorganisms composed of pelitomorphous calcite. In most specimens of dolomites, relicts of an organogenic-clastic lumpy texture of original limestones can be distinguished. The replaced organic remains are found only in fine- and medium-grained dolomites while coarse-grained dolomites (0.45-0.60 mm) are free of organism remains.

Determining the postsedimentary origin of dolomitization of the limestone and their dolomitic cement is just the first step in understanding the genesis of these dolomites.

An analysis of the geological structure and hydrogeology of the region indicates that the source of magnesian solution was a thick Jurassic bed northeast of the deposit, which forms the central part and the southwestern slope of the Caucasus range (see Fig. 1). The Jurassic was formed in continental conditions and contains tectonically separated coal-bearing areas of Tkvarcheli deposit. Besides the coal seams, the upper horizon of the porphyritic suite contains evaporites, with gypsum beds and interlayers. In the gypsum-bearing evaporitic

beds, magnesite is always present [3]. An additional source of the magnesium could be coal seams which contain lansfordite $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ and nesquehonite $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. The evaporitic formations of the Caucasus geosyncline are distinguished by a high mineralization of groundwater, up to 300 g/kg [2].

Based on full chemical and quasiquantitative spectral analyses of limestones and dolomites, we have calculated the balance of material redistribution in the course of transformation of limestone into dolomite. It was determined that in the course of dolomitization TiO_2 , K_2O , P_2O_5 , remained stable, where these oxides were introduced, %: SiO_2 0.01; Al_2O_3 0.05; Fe_2O_3 0.46; FeO 0.14; MnO 0.01; MgO 12.81; trace elements, g/ton: B 16.8; Ba 6.9; La 3.3; Zr 0.4; Ni 0.2; extracted from dolomites were the oxides, %: CaO 16.06; Na_2O 0.06; and trace elements, g/ton: Zn 105.8; Sr 59.1; Cr 4.3; Pb 5.1. The balance shows that, in addition to large amounts of magnesium, the solutions contained iron and manganese oxides, silica, and alumina (probably as clay colloids), boron, barium, lanthanum, zirconium, and nickel. The geochemical connection between boron and silica and iron, and in particular boron concentration by fine crystalline and amorphous iron oxides and hydroxides, have been described by many investigators [15, 23, 37, 39]. In addition, Strakhov [32] demonstrated that intensive chemical weathering of primary rocks on watershed areas destroyed all complex silicate and sulfidic, magmatic, and metamorphic minerals, while the components Fe, Mn, P, V, Cr, Ni, Co, and other elements passed into the solution and partly migrated in this form, while partly they were sorbed by micelli of clay minerals, and transported as suspended matter. Boron is a mobile element in aquatic solutions, and drying salt-bearing basins are usually enriched in it [24]. It is brought into solution by weathering and volcanic eruptions [9]. Barium is easily brought into solutions in continental sediments, and usually is also mobile. The sources of lanthanum, zirconium, and nickel could also be Jurassic effusives.

The groundwater of the continental Jurassic, with the characteristic trait of absence of aquifer horizons (A. G. Popov, personal communication) migrated in the southwestern direction toward the Black Sea; along the line of the lateral thrust, their path was barred by intensively dislocated overturned lower Jurassic limestone mass. The limestones contained mostly alkaline water, while the Jurassic migrating water was nearly neutral or acid composition, and contained the above chemical components. In the zone of water mixing arose an alkaline geochemical barrier, which was the cause of dolomitization, promoted also by high cracking and abundant fractured zones in carbonate rocks [11].

The dolomites were formed in the area of geochemical barrier in the following sequence: first limestones were dolomitized as some of their calcium ions were replaced by magnesium. These limestones eventually became the small- and medium-grained dolomites of the first generation, with typical organogenic replacement remains, skeletal limestone "shadows," and zonality of rhombohedral crystals. The limestone dolomitization was promoted by the magnesian calcite in their mineral composition, which was readily replaced with dolomite. According to the classical replacement reaction, calcium is removed from limestone during dolomitization in the form of a solution and reacting with remains of magnesium in the initial solution or in new portion of the solution, is synthesized into coarse-grained dolomite with distinct transparent crystals, free of any limestone replacement structures or any inclusions resembling microfaunistic remains. The chemogenic dolomite of the secondary generation, as it was precipitated, cemented the clastic dolomites of the first generation formed by limestone replacement, and created the parts of the ore body of the Tkvarcheli deposit highest in magnesium. It is this chemogenic dolomite that is distinguished from the replacement dolomite by light pink color, high magnesium content, higher silica, alumina, and iron hydroxide contents, and the trace elements not found in limestones.

By the set of features, such as the shape of the body of the mineral deposit and its correlation with the enclosing rocks (the dolomitization front), the texture (size, habitus, and zonality of crystals), the structure (the degree of spottiness and stratification), the rock chemistry (Sr, Na_2O), the mineral composition (the presence of protodolomite and magnesian calcite), and contents of noncarbonate impurities (including clays), the trace elements and their proportions, as well as the presence of limestone organic remains replaced by dolomites, the dolomites of this deposit should be classified as secondary, or epigenetic dolomites formed as a result of the action of high-magnesium low-temperature solutions, which altered previously solidified limestones that had passed through metagenesis and tectonic reworking. The presence of a second generation of dolomititic mineral formed by synthesis of calcium washed out of limestone with residual magnesium of the solutions and its crystallization complicates the general picture of formation of the commercial bed. Two subsequent

phases can be identified in its genesis: the replacement of magnesian limestones by dolomite, and the reaction of the displaced calcite with the remaining magnesium in the solution with simultaneous synthesis of chemogenic dolomite, which cemented the replacement dolomite.

The study has thus determined the existence of a new commercial chemogenic-metasomatic genetic type of dolomite deposit, which until now has never been described in the literature or included in the existing classifications [4, 13].

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CARBONATE BRECCIAS AT THE UPPER CAMBRIAN/LOWER ORDOVICIAN BOUNDARY
ALONG THE BATYRBAI VALLEY IN THE LESSER KARATAU

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UDC 552.54:552.511(574.5)

Carbonate breccias are described which make up a significant portion of the Batyrbai section in the Upper Cambrian and Lower Ordovician and the Lesser Karatau ridge. Based on textural and structural features, four morphological types of breccia are distinguished. The assemblage of indications such as the breccia type, the composition and textural-structural features of the country rock, and the interrelationships of breccia lenses and country rock have permitted us to decipher the mechanism of the breccia's formation. Genetic interpretation of the breccia has allowed us to establish the various conditions of their accumulation.

The section of carbonate deposits in the Shakbakta suite of the Tamdy series along the Batyrbai valley in the Lesser Karatau is well known as a possible stratotype for the boundary of the Cambrian and Ordovician systems [1, 2, 5, 9, 10]. It is well exposed, is composed of steeply dipping layers of limestones and dolomites and slightly disrupted faults, and is characterized by a fauna mainly of trilobites, conodonts, and brachiopods.

One of the essential elements of the section is the carbonate breccias, a description of which is provided in this work.

The carbonate breccias throughout the section of the Batyrbai valley are made up of lenses and strata which are sharply differentiated from the layered limestones and dolomites in the form of massive beds (Fig. 1). In the lower 350 m of the section, they form about 30 lenses and strata totalling 90 m in thickness, varying in individual lenses from dozens of centimeters to 15 m. The breccias represent clasts (fragments) of small calcareous layers cemented with a green carbonate matrix.

The carbonate rocks enclosing the lenses and layers of breccia are extremely varied. The section is made up of dark gray nodular and wavy-bedded limestones, platy, parallel-bedded, fine-grained limestones with a microgradational structure, massive coarse-platy calcareous sandstones (calcarenites) and coarse-platy calcarenites with a graded structure, and massive light gray dolomites. At individual stratigraphic levels, the breccias associate with algal bioherms. A comparison of the composition of the layered carbonate rocks and clastic material in the breccias yields evidence of their similarity. This permits the assumption of an intrabasinal source for the clastic material, as well as comparable times for the processes of accumulation, disintegration, and redeposition of the sediments.

The shape of the breccia clasts varies from platelike and tabular to angular and rounded (Fig. 2). In cross-section, the platy and tabular clasts have the form of elongated rectangles.

Based on the composition of the clasts and their cementing matrix, three groups of breccia may be distinguished (Table 1), with: 1) clasts of primarily parallel-bedded limestones, with a granular carbonate (calcite-dolomite) matrix, 2) clasts of primarily wavy-bedded limestones, with a granular carbonate matrix (Fig. 3a, b, c, f, g), and 3) clasts of algal and wavy-bedded limestones, with a granular dolomite matrix (see Fig. 3d, e).

Definite regular patterns are observed in the texture of the breccia lenses and strata which are caused by the distribution of the clastic material. These patterns are manifested in changes in clast shape, the relationship of clasts and granular matrix, clast orientation in relation to the top and bottom of the stratum, and clast size. Based on these parameters,

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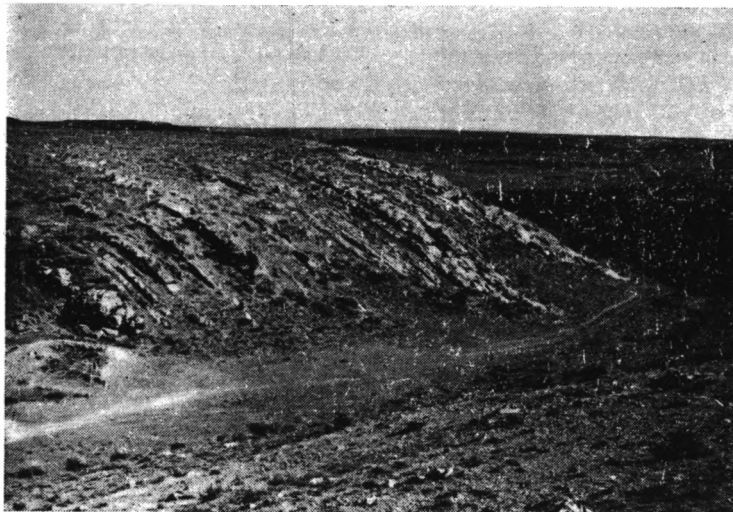


Fig. 1. General view of the lower part of the Batyrbai section; in relief, ledges of massive breccia beds are visible (member 3, 40-150 m interval).

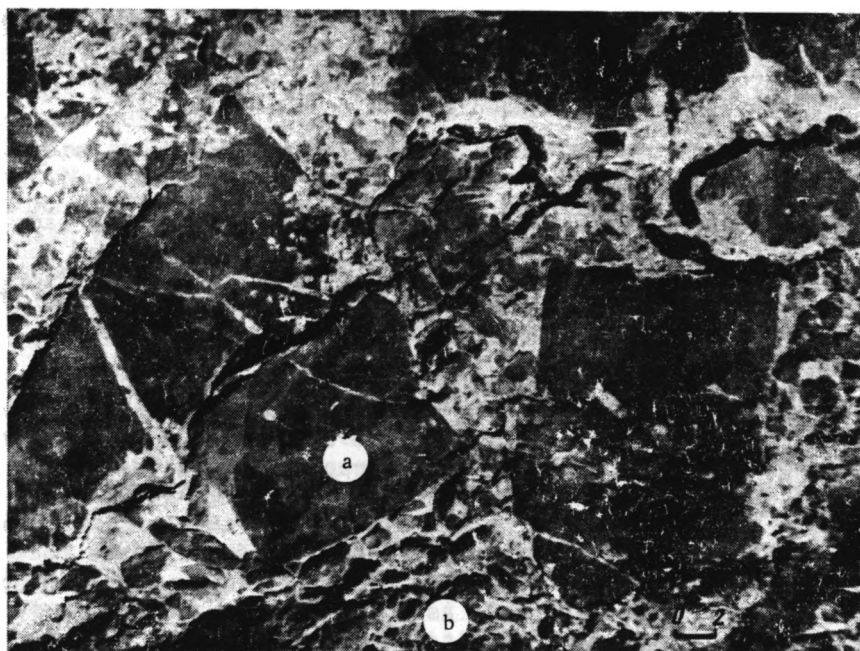


Fig. 2. Tabular and platy (a) and isometric (b) clasts in carbonate breccia; view of the bedding plane (member 2, reference marker 5 m; scale line, in centimeters).

the following types of breccia are distinguished (Fig. 4; see Table 1): 1) compact, formed of clasts layered like tiles, with platy and tabular shape, subconcordantly oriented relative to the top and bottom of the stratum (Figs. 5a, 6c); clast size along the long axis varies from 0.05 to 0.5 m; 2) framework, composed of platelike, tabular, and angular clasts with arbitrary orientation, which form a dense framework of rock, with a granular matrix filling the interstices (see Figs. 5c, 6a); clast size varies within a brief range of a few to dozens of centimeters; 3) floating, characterized by the predominance of a granular matrix in which oriented clasts with tabular, angular, or rounded shape are scattered ("float") in the matrix and do not have mutual contacts; the size of the clasts is 0.03-0.1 m, more rarely a few dozen centimeters; 4) sorted, distinguished by clasts which are both fine and comparatively uniform in size with angular and ellipsoidal shapes, with subparallel orientation relative to the stratum roof (Fig. 7). In individual lenses and strata in the breccias, coarse exotic boulders and lumps of massive calcarenite and algal limestone are noted. The majority of the

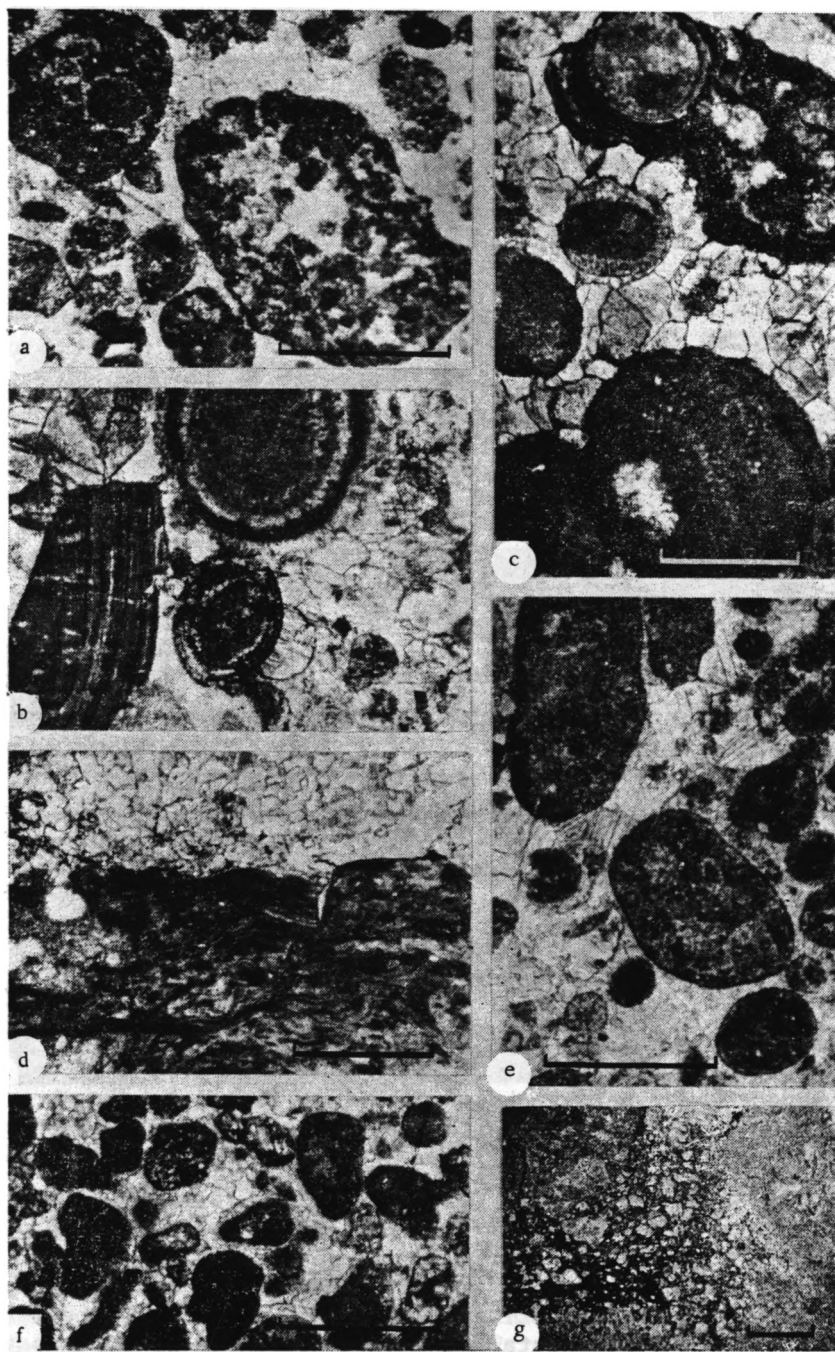


Fig. 3. Granular-carbonate matrix of carbonate breccias: a, f) Micritic and aggregate grains of limestone in calcite cement; b, c) abraded grains of oolitic limestone in calcite-dolomite cement; d) nodule of algal limestone (indicated by arrow), included in dolomitic cement; e) grains of microgranular limestone, included in calcite-dolomite cement; g) calcite-dolomite matrix with fine, scattered clay material (length of scale line 1 mm).

TABLE 1. Morphological and Genetic Classification of Carbonate Breccias along the Batyrbai Valley

Type of clast component	Composition of clasts and matrix									
	parallel-bedded limestones; matrix granular carbonate			wavy-bedded limestone; matrix granular carbonate				Algal and wavy-bedded limestones; matrix granular dolomite		
	1*	2	3	1	2	3	4	3	4	
Sorted	+	+	—	+	+	—	—	—	—	
Floating	+	—	—	+	—	—	+	—	—	
Framework	+	—	+	+	—	+	+	+	+	
Compact	+	+	+	+	+	+	—	+	—	

*Classification of flows by origin: 1) debris, 2) grain, 3) landslide-creep, 4) storm; +) breccia type traceable in section, -) not traceable.

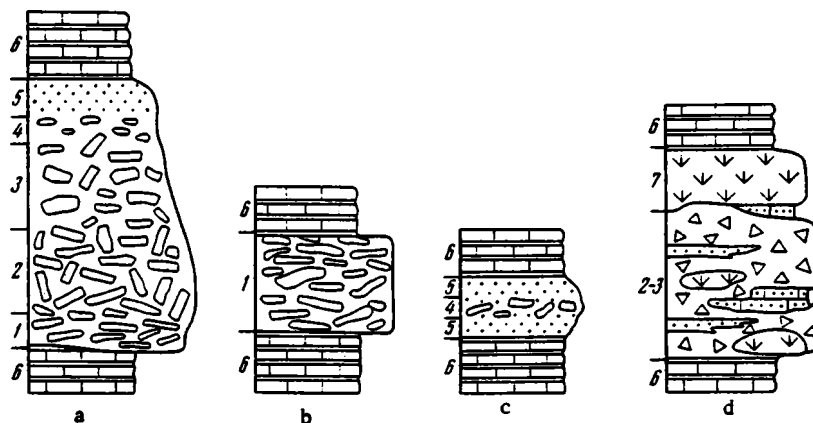


Fig. 4. Types of carbonate breccia in the Batyrbai section. Genetic types: a) deposits of debris flows (olistostromes), b) landslide-creep deposits, c) deposits of grain flows, d) storm deposits (wave-break deposits). Morphologic types: 1) compact, 2) framework, 3) floating, 4) sorted, 5) calcarenites, 6) bedded country rock, 7) massive algal bioherms (not to scale).

breccia lenses and strata include isolated rhythms composed of calcarenites which either begin or conclude the breccia rhythms. They sometimes even out irregular surfaces in the latter (see Fig. 5c). In other cases, the breccia strata underlie massive bioherm structures made up of algal (epiphyte) limestones (see Fig. 4d).

The types of breccia enumerated at different stratigraphic levels in the section make up lenses and strata, occasionally forming sequential transitions from one type to another. An overall gradational sequence of types is observed as (see Fig. 4a): compact (1)...framework (2)...floating (3)...sorted (4)...calcarenites (5). Occasionally some one of the types falls out, and the series is represented in the form of an abbreviated sequence: 1-2-4-5 or 2-3-4-5, etc. Moreover, strata and lenses are present which make up only one type, compact (see Fig. 4b) or sorted with a gradational series 5-4-5 (see Fig. 4c), or else combined framework and floating (see Fig. 4d).

Different types of breccia are distributed unevenly throughout the section, with distinct patterns evidently associated with the evolution of the basin. The characteristics of the section are presented on the basis of the data from this author and other investigators [1, 2, 10].

Member 1 (from -60 to -36 m)* is composed of thin platy, wavy-bedded limestones. In this member, eight breccia lenses and strata are noted, from 0.5 to 2m thick. The large

*The minus sign is used to mark the portion of the section lying below an arbitrary zero marker [1, 10].

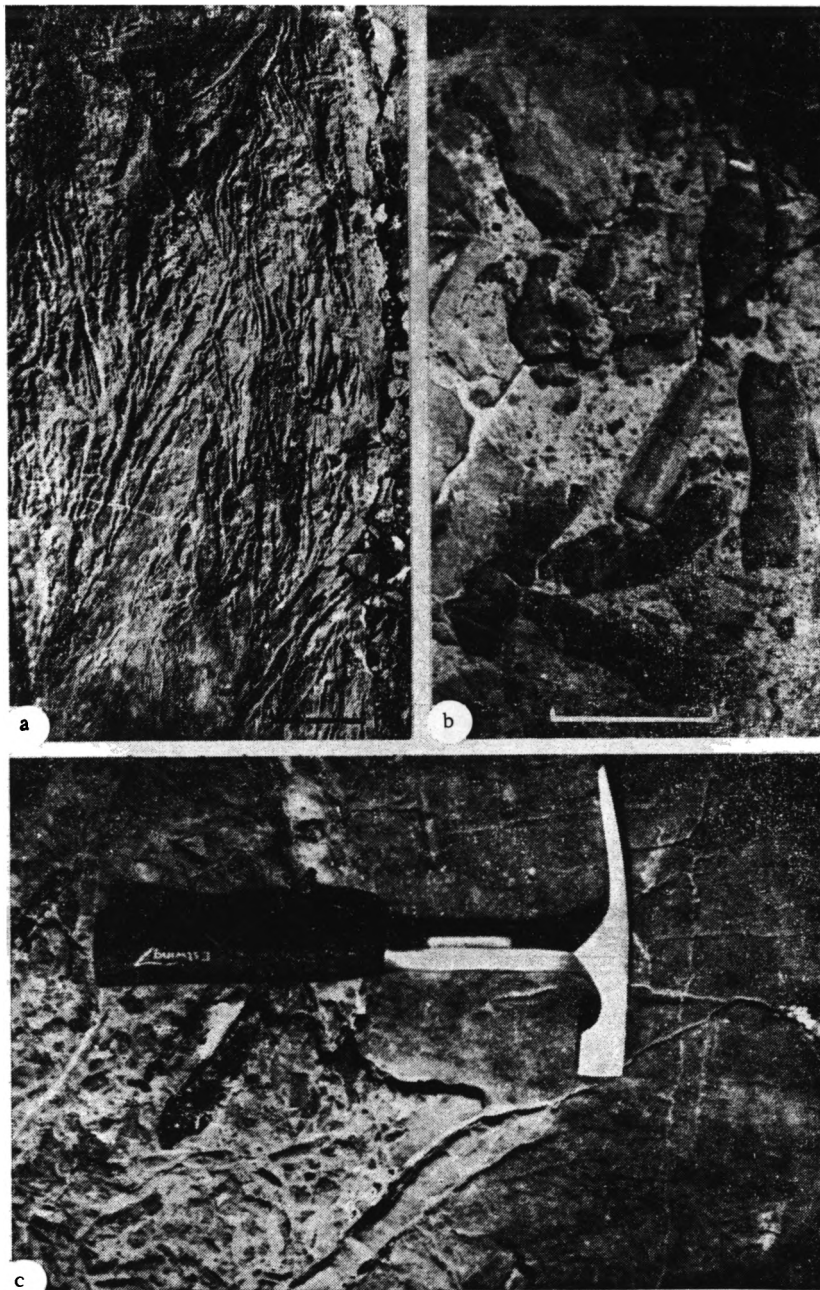


Fig. 5. Morphological types of breccia: a) Compact type of breccia in landslide-creep deposits; distinctly evident is the tilted bedding of the clasts, subparallel to the base of the stratum (member 2, interval from -18 to -16 m; length of scale line 0.2 m); b) framework breccias in debris-flow deposits (member 2, reference marker -5 m, length of scale line 5 cm); c) breccias of the sorted type transitional to calcarenites. In the center of the photo, a large clast emphasizes the standing-wave structure. The head of the hammer is pointed toward the top of the stratum (member 2, reference marker -21 m).

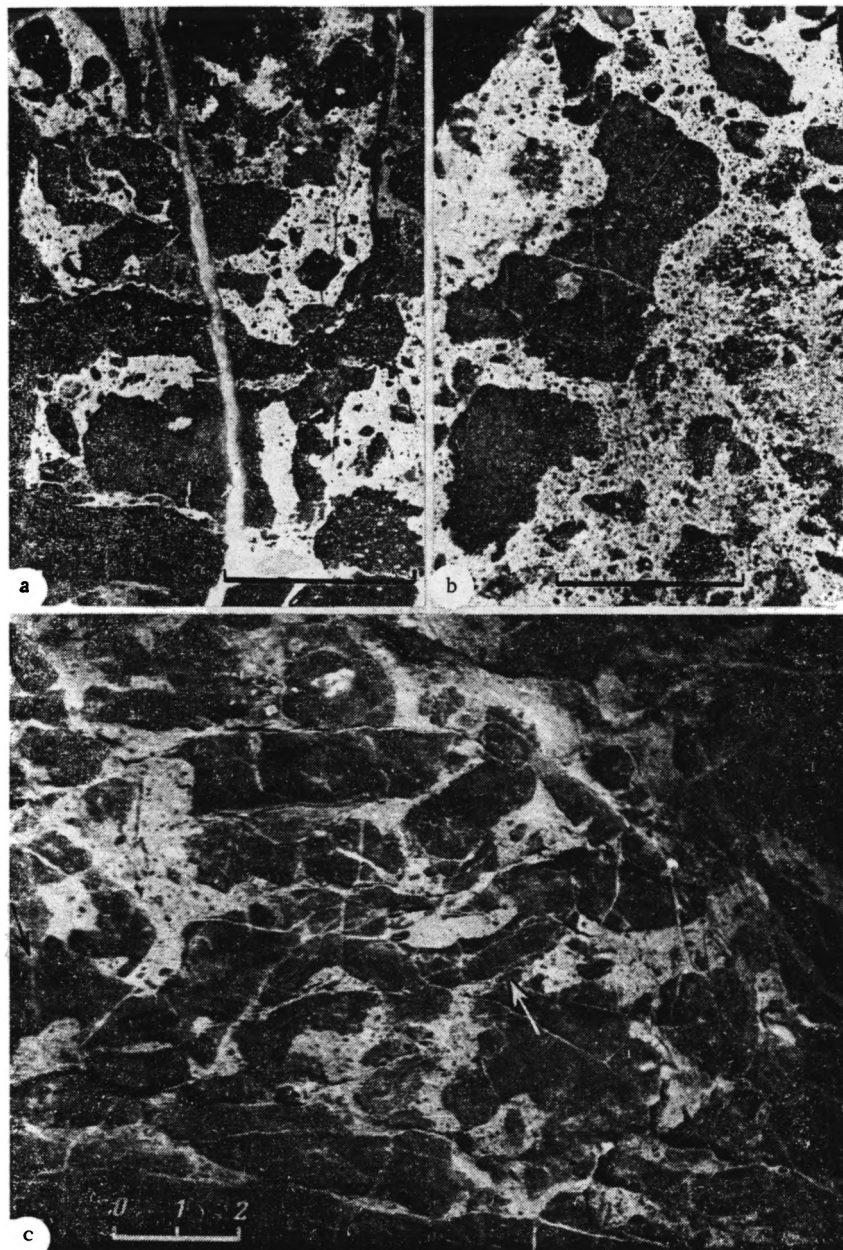


Fig. 6. Morphological types of breccia: a) Framework breccias in storm deposits (polished section, member 5, length of scale line 3 cm); b) floating breccias from storm deposits (polished section, member 4, reference marker 260 m, length of scale line 3 cm); c) compact type of breccia from landslide-creep deposits. Arrows indicate plastically deformed clasts, evidence of incomplete lithification of the sediment at the time of disintegration (member 3, 6.5 m interval, scale division in cm).

lenses are characterized by gradations of the type 1-2-4-5. Smaller lenses and strata are made up of compactor sorted breccias with the 5-4-5 gradation.

Member 2 (from -36 to 0 m) is made of fine-grained, parallel-layered limestones with micrograded bedding. Among these rocks, strata are often noted of coarse-platy calcarenites with graded bedding. Here ten lenses and strata are traceable of well differentiated breccias with the gradations 1-2-3-4-5, 1-2-4-5, 1-2-5, and 5-4-5. Their distinguishing feature is the predominance of clasts with a platelike shape. The thickness of the breccia layers varies from 0.5 to 10-15 m.

Member 3 (from 0 to 103.4 m) is composed of wavy-bedded limestones and coarse-platy massive calcarenites. Breccia strata and lenses at distinct intervals in the section in this

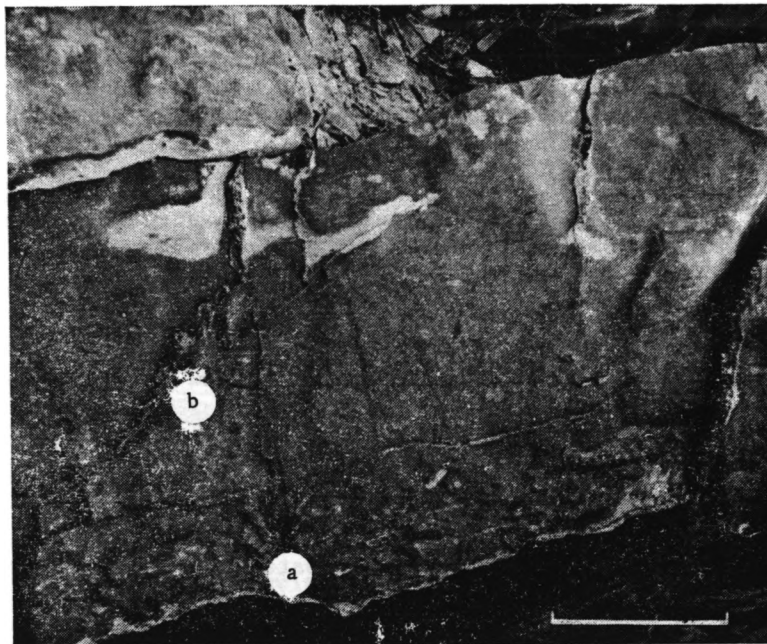


Fig. 7. Sorted breccias in a grain flow; breccia (a) and calcarenite (b) grading rhythms (length of scale line 0.1 m).

member differ sharply from one another. At the base of the member (the interval from 0 to 35 m), the breccias represent only one compact type, and only one stratum (the 11-14-m interval) has an expressed gradation of the series 2-3-5. The thickness of the lenses and strata is 1-3 m; the 40-60 m and 70-89 m intervals include lenses and strata with extremely disordered clast orientation. Massive and coarse-platy calcarenite strata up to 1 m thick wedge out into the breccia lenses, in which framework and floating types are distinguished. In tracing these breccias long the strike, an inconsistency is noticed in the volumetric relationships of the clasts and granular matrix, lensitic coarsening, and sharp wedging at the contact with the country rocks. Also characteristic is the presence of small rounded bodies (calipters) of algal limestone (see Figs. 3d, 4d). The lenses are in some cases covered with massive algal bioherms. The thickness of individual lenses is 1-1.5 m. The total overall thickness of the members consisting of densely unloaded lenses is 10-15 m, the 60-79 m and 89-103.4 m intervals are made up of variously shaped nodular and wavy-bedded limestones, sometimes with small-scale oblique bedding. Strata of coarse platy calcarenites quite frequently interstratify wavy-bedded limestones. The breccia strata and lenses are thin and rarely reach 1.5-2 m. In one case, the breccias have a gradation in the series 2-4-5; breccias of the sorted type are present here, enclosed within coarse-platy calcarenite strata with either an oscillating or an inverse gradational structure of the series 5-4-5. The thickness of these lenses and strata is 0.2-0.5 m.

Member 4 (103.4-168 m) is composed of microgradational and wavy-bedded limestones. Lenses of carbonate breccias subdivide this interval into approximately equal parts with a thickness of 7-10 m each. Grading is practically absent; framework and floating breccias predominate. The clasts are uniform in composition and represent fragments of wavy-bedded limestone layers. In certain lenses (the 124-126 and 146-149 m intervals). Lumps of algal limestones are observed. The base of these lenses cuts the roof of lower-lying bedded rocks.

Member 5 (168-300 m) is composed of dolomites and limestones with different textural and structural indications. On the whole, this interval is represented by the rhythmic alternation of packets every 5-10 m. Each rhythm is crowned by massive carbonate breccias with clasts of algal and wavy-bedded limestones. With a uniformity of composition, the breccias in this member have different structures. At some intervals (181.5-193, 198-205; 288.5-289.5m) clear indications of gravity redeposition are observed - abrasion of the roof of lower-lying deposits, the presence of huge exotic lumps of algal limestone, microfolds of plastic flow. Characteristic of breccias at the intervals 192-194, 223-226, 238-239, and 256.5-260 m are weak sorting, a direct dependence of clast and matrix composition on the composition of underlying bedded rocks, and the presence of unaltered algal bioherms overlying them. The thickness of the breccia lenses is 1.5-2 m.

Accumulation of coarse clastic carbonate deposits in stratified beds is usually associated either with zones of shallow water above the wave base, when sedimentation is determined by depth sufficient to penetrate active wave action [3, 16], or with zones of deeper water, in which sedimentation was caused by gravity redeposition of slightly lithified sediment along the basin slope [6, 7, 12, 14, 15, 18].

The sharply differing circumstances of coarse clastic carbonate material presuppose differences in the processes of their deposition, as well as in the structural and textural features of the sediments which formed them and their material composition.

In the literature, primarily the foreign literature, classifications are well known for carbonate breccias based on various parameters. According to the data of Cook and Taylor [11], carbonate breccias with deep-water and mixed (shallow and deep water) material are differentiated according to the clast material. Krause and Oldershaw [11] proposed a classification based on a method of grouping the clasts and on the nature of their gradational distribution. Based on the composition and structural-textural indices, different zones are distinguished under conditions of piedmont-slope sedimentation (ledge, canyon streams, under-water debris fans).

A genetic interpretation of breccias in the Batyrbai valley section is constructed on the hypothesis that their formation in shallow- and deep-water zones in the basin was differentiated by the time of accumulation of clastic material. In shoaling zones above the wave base, clast accumulation occurred episodically during severe storms, which eroded slightly lithified bottom sediment. In a period of sharp abatement in the energy of the water mass at the surface of such lenses, small bioherms of calcareous algae or stromatolites could grow (see Figs. 3d, 4d), a fact which is also observed in other sections in the Shabakta suite of the Lesser Karatau [4]. Alternation of periods of high and low energy states in the aqueous medium determined the features of structure and texture in such breccias. They bear no indications of gravity redeposition, which is spatially associated with algal bioherms; the composition of their clasts depends on the composition of the surrounding rocks. In tracing the breccia lenses along the strike, an inconsistency is noted in the volumetric ratios of clasts and granular matrix, lensitic unloading, and wedged joining at the contact with the country rock. At the base of the breccia lenses, small-scale, slightly inclined unconformity surfaces are observed. Any type of clast sorting is absent; the breccias are represented by framework or floating types or a combination of them (see Fig. 6a, b). The features mentioned above characterize breccia lenses and strata of member 3 at the intervals of 40-50 and 70-89 m and member 5 at the 192-194-, 223-226-, and 256.5-260-m intervals.

The assemblage of indices in breccias of these intervals in the section is evidence of the redeposition of disintegration material practically in situ, which permits them to be considered breccias of storm deposits in the central zone of the carbonate shelf (see Table 1 and Fig. 8d).

Under conditions of a relatively deep-water portion of the basin, sedimentation was defined by the redeposition of clastic material by gravity flows from relatively shallow-water zones, whereby the entire mass of the breccia layer could have formed simultaneously [12]. The structural and textural indices of such deposits confirm the special physical properties of the flow of a non-Newtonian fluid - a laminar regime, dispersion tension of the grains (the Bagnold effect), and turbulence. These properties produce the mechanism of the "bearing capacity" of the flow, by which redeposition of coarse clastic fragments is accomplished over distance [12, 15, 18]. It has been established that the most important sedimentological parameters defining the conditions of deposit accumulation in gravity flows are the slope of the bottom, the heterogeneous composition of the bottom sediment, the critical mass of the sediment, and the action of external forces which destroy the stability of the sediment (waves, seismic pulses) [7, 8, 12-14]. With movement of the sediment flow along the slope, different regimes are possible, from laminar to turbulent, depending on the composition, bottom inclination, and distance over which it was displaced [14, 15, 18]. Classification of modern sedimentation by gravity flow [15, 17] are based on these regimes, with subdivision of several types: landslides, creep, debris flow (flow of fragments), grain flow, fluid flow, liquid flow, turbulent flow. Fisher [12] noted the following indices for gravity-flow deposits: graded distribution of clasts with both direct and reverse gradation, poor sorting of material, parallel orientation of clasts relative to bedding, channel forms of the bottom. Such deposits are well known in the literature as olistostromes, autokinetic deposits, and gravity mixtures [5, 7, 8, 18].

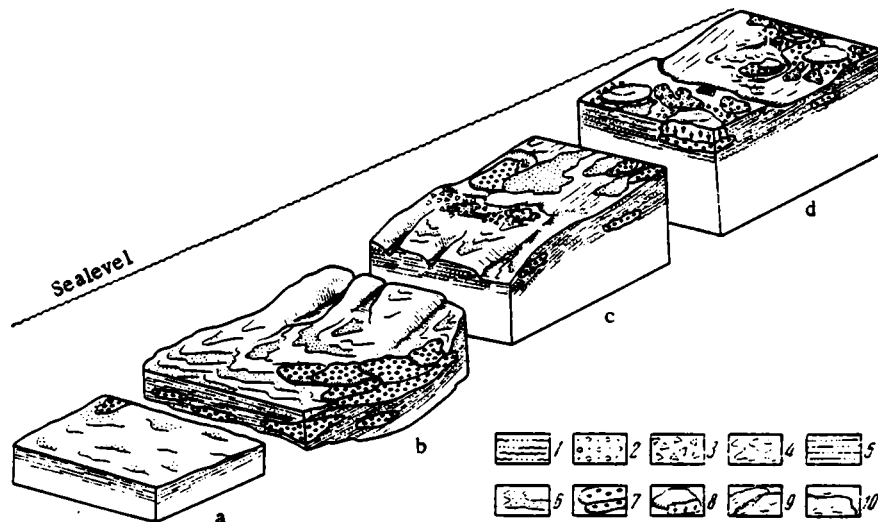


Fig. 8. Model of breccia accumulation conditions throughout the Batyrbai valley: a) Basinal depression, b) slope and piedmont slope (carbonate ramp), c) outer portion of the carbonate shelf, d) central portion of the carbonate shelf. 1) Wavy-bedded limestones, 2) massive, indistinctly bedded calcarenites, 3) storm-deposit breccias, 4) parallel-bedded microgradational limestones (distal calcoturbidites), 5) same, in the section, 6) calcarenites with graded bedding (proximal calcoturbidites), 7) carbonate breccias from gravity redeposition (landslide-creep, grain and debris flows), 8) bioherms of algal limestones, 9) underwater rivers (canyons), 10) underwater ledges.

Based on the observed structural and textural indices of gravity-flow breccias throughout the Batyrbai valley, it may be supposed that they were laid down by flows with liminar, dispersion, and liquid regimes. The liminar flow regime formed the compact and framework types of breccia (see Fig. 5a, b; 6c), the liquid regime formed the floating type (see Fig. 4a), and the regime of dispersed tension the sorted type of breccia (see Fig. 4a, 5c, 7). The varying level of structural and textural maturity deserves attention (the degree of graded sorting) in the breccia lenses, which is consistent with clast composition. The best developed gradation, represented by all types of breccia in the 1-2-3-4-5 sequence, is characteristic of member 2, which is made up of calcoturbidites. In the other members, dropping of one or several types is noted, with the development of gradational sequences of the 1-2-5, 2-5, 5-4-5, 2-3, etc. types. Apparently, structural and textural differentiation within the breccia lenses depends on the distance over which the flow was redeposited.

For members 1-3 (intervals 0-35, 60-70, and 89-103 m), the breccias may be interpreted as the deposits of clastic flow. Characteristic of these are direct and reverse grading of the clasts, poor deposit sorting, good preservation of structural features, erosion of the roof of lower-lying deposits (channel forms of the bed), linear orientation of clasts in upper and lower gradational rhythms in relation to the overall stratification of the bed, and reworked organic detritus. The well developed gradational sequence here for member 2 confirms significant dissection of the bottom slopes as well, while slightly differentiated breccias in members 1 and 3, deposited by flows in a liquid regime, apparently were laid down on lesser bottom slopes. Thin calcarenite strata at these intervals, with direct, reverse, and oscillating graded structures and with included breccia clasts of the sorted type, may be interpreted as deposits of grain flow. Breccia lenses with undeveloped grading (the compact type) and with traces of plastic deformation (see Fig. 6c) are landslide-creep deposits.

In members 1 and 3, the genetic features of the breccia lenses and strata and the nature of the surrounding rocks permit assumption of conditions in the outer portion of the carbonate shelf (see Fig. 8c). The calcoturbidite type of deposit in member 2 and the presence here of thick breccia strata and lenses with well developed clastic material grading is evidence of conditions either in the outer part of the shelf or on the piedmont slope and underwater debris fans (see Fig. 8a, b). Breccia lenses and strata in members 4 and 5 have in places distinct indications of gravity redeposition (the 124.5-126.6-, 145.5-150-, 181.5-183-, 288.5-289.5-m intervals). For the breccias in these members, conditions of the central portion of the carbonate shelf are proposed (see Fig. 8d). The formation mechanism of such breccias

includes disintegration of the bottom sediment by waves and sequential redeposition by creep under conditions of shoaling in a dissected zone of algal bioherms.

Thus, the study of the breccias in the Batyrbai section has shown that these formations are extremely varied in structural features and origin, which is associated with their accumulation under different facies conditions. Any indices taken alone does not permit a unique interpretation of the conditions of the environment. A genetic interpretation of the breccia strata and lenses is possible only on the basis of a comparison of the assemblage of indices, such as the composition of clasts and matrix, textural and structural features of the breccias, composition and structural-textural features of the country rock, nature of organic remains, and interrelationships of the breccias and surrounding rocks. Deciphering the mechanism of breccia accumulations of various types will provide important data for sedimentological and paleogeographic analysis.

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PALEOGEOLGY OF THE URAL-VOLGA REGION AND NORTHERN CASPIAN REGION
DURING KUNGUR POTASSIUM ACCUMULATION PERIOD

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The study analyzes the data on stratigraphic features, lateral occurrence, and size scales of sylvite, carnallite, bischofite, and polyhalite mineralization in Arta-Kungur halogenic formation of the Caspian syncline. The author comes to the conclusion that, at the beginning of the Kungur age, a system of subbasins of potassium sedimentation developed in this region; the subbasins were divided by archipelagoes of islands and shoals. The main sources of supply of the land-locked subbasins were marine and continental waters, which are described, indicating the principal directions of brine migrations between the subbasins.

During the Arta and Kungur ages of the Early Permian, the Ural-Volga and North Caspian regions encompassing the territory of the Caspian syncline, its northern and western borders, and the Sakmar-Belsk depression of the Ural foredeep were covered by a huge basin. It was a part of a system of Arta-Kungur and Kungur basins of evaporitic sedimentation of East European platform; in this system, it was the main terminal component supplied mainly by seawater from the preparatory basin of the Moscow syncline [8].

The paleogeology of the region occupied by the terminal Caspian Basin and its coastal areas has been described in general terms, on the basis of studies and generalizations of vast factual data. It has been established that for the larger part of the Kungur age, this basin was the only one, and that its initial segments in tectonically subsided areas inherited since the Arta age were relatively deep. During the Kungur time the basin gradually became shallow, turning into a system of shallow, but large, water bodies stretching for hundreds of kilometers. In these water bodies, whose location was determined by inherited tectonic troughs and depressions in the relief of the surface of previously accumulated sedimentary strata, potassium sedimentation took place periodically. In the final intervals of the Kungur age, the terminal basin, progressively more isolated and shallow, was transformed into a system of semiisolated water bodies, which disappeared at the end of the Kungur time [7]. In addition to the seawater, which flowed from the preparatory basin at the north, this terminal basin was fed by continental waters brought mainly from the Ural mountains by rivers and seasonal torrents. Some of these, probably inherited from the Arta time, could remain powerful through the earlier half of the Kungur age. A certain amount of continental waters, probably in underground streams, was brought from the huge continent lying to the west of this area [11].

It is assumed [2] that during the potassium accumulation, the aquatorium was divided by large rises, and the sedimentary bed forming its floor was crumpled into anticlines of different amplitudes, conducive to development of semiisolated tanks. The contours and relief of the basin floor in that period was affected by chains of local rises, which crowned the western and northern side ledges of the Caspian syncline, and presented buried biohermal structures (which on the western ledge were locally made of reef material) of the Asselian-Sakmarian age (in the western ledge) and Arta age (in the northern ledge). The influx of terrigenous matter into the basin came not only from the shores, but also from the inner areas. One such area was situated in the central parts of the eastern half of the syncline.

This general picture of the paleogeography of the region during the Kungur time can be made more specific and detailed on the basis of the available data of the studies of geological structure of Arta-Kungur halogenous formation of the Caspian syncline and the accumulation patterns of its component units, as well as more recent data.

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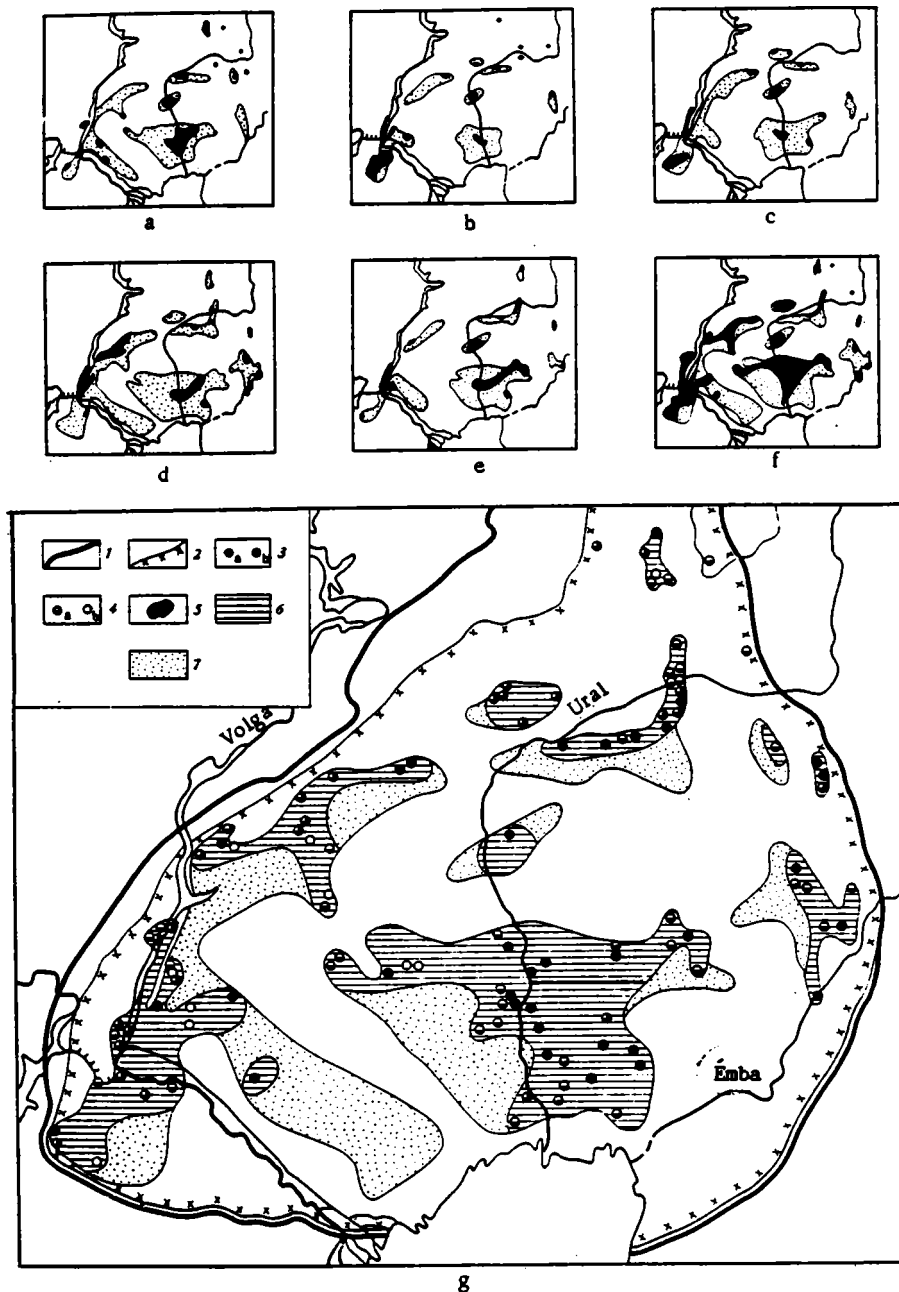


Fig. 1. Sylvinites and sylvinitic rocks in Ural-Volga and North Caspian regions in Ulagan layers: a) cycles III, b) IV, c) V, d) VI, e) Elton layers, f) upper Irensk subhorizon, g) 1-2 - rock occurrence boundaries (1 - gypsum anhydrite, 2 - salt rocks of Kungur stage); 3-4 - boreholes drilled through the profile of upper Irensk subhorizons, beds: 3 - rocks mainly consisting of the mineral, 4 - rocks containing the mineral (a - core, b - geophysical data), 5-6 - territories of proven occurrence of rocks consisting mainly of the mineral and rocks containing the mineral (5 - for Figs. a-f, 6 - for Fig. g), 7 - hypothetical occurrence territory of these rocks.

A review of the published materials [3, 4, 9, etc.] and new information on the geological structure, lithologic-facies composition, and potassium contents of this formation, accumulated by the mid-1970s, made it possible to accomplish three tasks:

- develop a detailed stratigraphic map of the Kungur stage of the lower Permian of the Ural-Volga and North Caspian regions [5, 10];

- determine the basic regularities of the stratigraphic confinement and lateral occurrence in this formation of accumulation of chloritic and sulfatic potassium salts and bishofite [1, 5-7, 11]; and

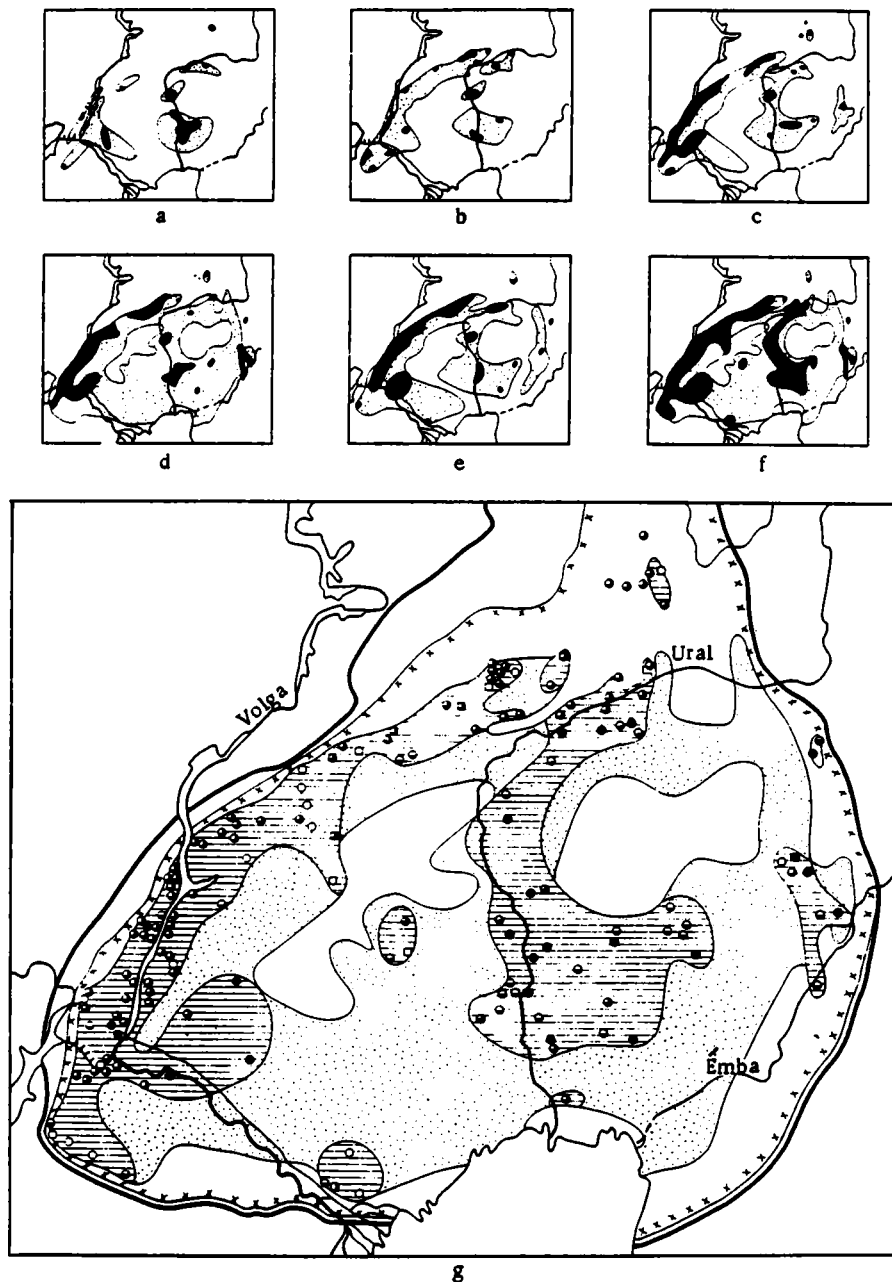


Fig. 2. Maps of occurrence of carnallite and carnallite-containing rocks in Ural-Volga and North Caspian territories. Notations as in Fig. 1.

— clarify the general patterns of accumulation of these salts (or their ingredient components) and the evolution of the evaporitic process in the Kungur basin on the territory of the Ural-Volga and Northern Caspian region [1, 5-7, 11].

According to the stratigraphic map that has been developed, the Kungur stage was divided, as in the classical scheme, into Filipov (lower) and Irensk horizons; in the latter, lower and upper Irensk subhorizons were identified, with the upper subhorizon divided (from bottom to top) into Ulaga, Elton, Chelkar, and Inderbor layers, encompassing cycles I, II-VI, VII-X, and XI-XIII, respectively. These stratigraphic subdivision, or many of these subdivisions, have been traced in hundreds of profiles by mean of layer-by-layer correlations.

The following facts were determined: 1) chloride potassium sedimentation began in the Filipov time, and achieved its peak (in area and magnitude) in the second half of the Elton time; it was quite limited and narrowly local later, with sylvite deposition gradually giving way to carnallite deposition; 2) polyhalite mineralization was developed mainly (in area and

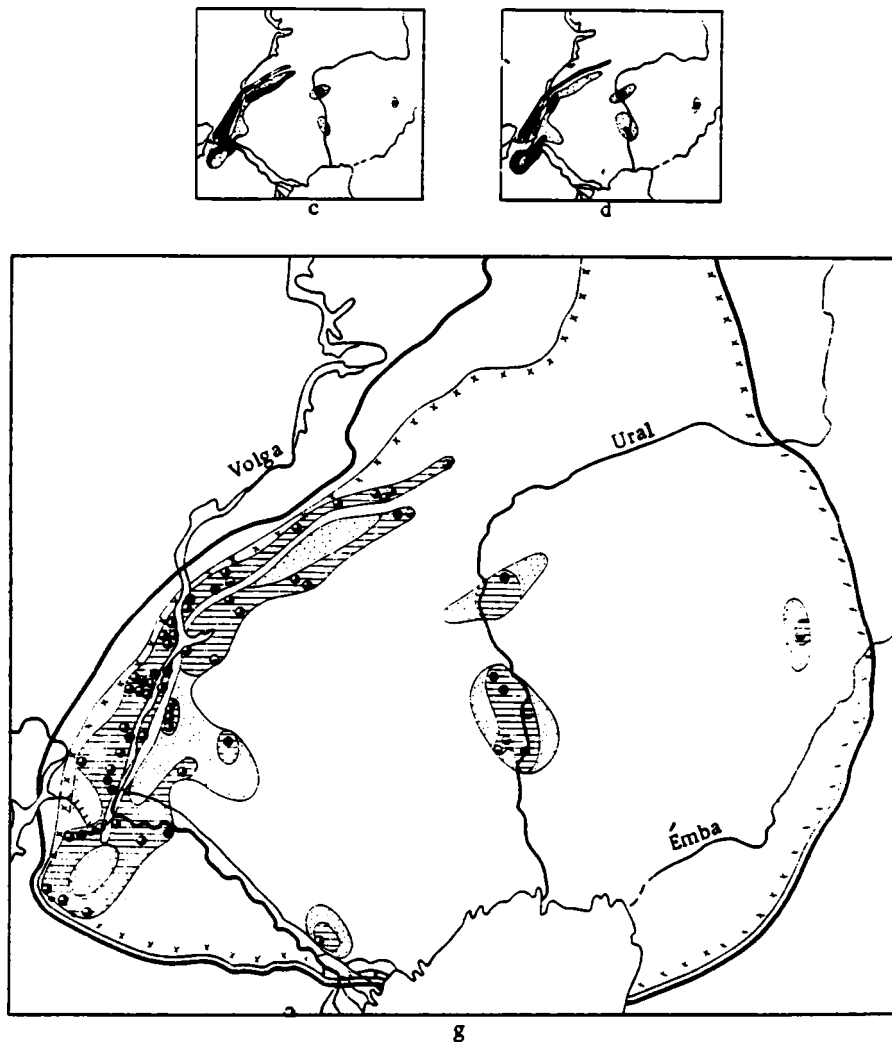


Fig. 3. Bischofite and bischofite-containing rocks in Ural-Volga and North Caspian territories. Notations as in Fig. 1.

magnitude) in the lower third of the upper Irensk subhorizon, and starting from the upper cycles of the Elton layers, became much less intense; 3) polyhalite was formed in those portions (zones of the evaporitic basin) of halogenous formation where large amounts of sulfate ions and other polyhalite ingredients could be brought, in addition to those in the brine flowing from the preparatory basin. The main source of these additional portions was continental water flowing from the Ural Mountains, plus water drained from the western land areas.

The paleogeography of the region, and especially locations of potassium sedimentation basins, sources, and directions of flow of marine and continental waters into them, was clarified in mid-1970s by a series of schematic maps of occurrence, in narrow stratigraphic intervals of the upper Irensk subhorizon, of sylvite, carnallite, bischofite, and polyhalite rocks [6, 11].

In recent decades, a lot of new, only partially published materials [2, and others] on geologic structure and potassium occurrence in Arta-Kungur halogenous formation of the Caspian syncline have been obtained. Studies of the tectonics of the syncline and its surroundings yielded an updated schematic map of the tectonic zones of the Caspian depression and its surroundings [2]. With this map, one can trace with confidence and in detail the paleotectonic and paleogeographic settings of potassium accumulation in the terminal basin of the Caspian region.

The previous and new factual data and a review of published maps, in close correlation with the modern views of the regional tectonics, made it possible to refine, in some cases substantially, and to augment the earlier notions of the stratigraphic correlations, the

occurrence areas, and the magnitudes of development in the Arta-Kungur halogenous formation, of sylvite, carnallite, bischofite, and polyhalite mineralization, as reflected in the new four series of schematic maps (Figs. 1-4). These maps include most of the available information on potassium structures and profiles of the formation, namely, 153 drilled salt domes and anticlines in the Caspian syncline, and more than 520 profiles or boreholes in the western, northwestern, and northern surroundings of the syncline and in the Salmar-Belsk depression. The analysis of the data represented in these maps clarifies the evolution of potassium and bischofite sedimentation in the area during the late Irensk time, and also the pattern of distribution of polyhalite formation; it also provides a starting point for a detailed paleogeographic mapping of this region for the Kungur potassium accumulation time (Fig. 5).

Within the territory, later covered by the aquatorium of the Caspian Kungur terminal basin in the Early Permian Sea, long before the beginning of the Kungur age, there were relatively deep sea zones controlled by Volga, Krasnokutsk-Ozinkov, Utvino-Ilelsk troughs, and other large negative structures, including probably the zone controlled by Chelkar and Inder depressions. In the late Arta time, carbonate-clay sediments accumulated in the depressions. These large and deep lows of the relief were inherited into Kungur time, and gradually were leveled by accumulating thick halite strata; judging by the differentiation of the salts of different composition with respect to the side of the Kungur terminal basin, these differences were reflected in the seafloor relief until the end of that period. This made possible the separation, within the terminal basin, even during the late Irensk time, of autonomous subbasins of potassium sedimentation, which initially appeared as relatively deeper tanks. These tanks were separated by increasingly more distinct shallow-water areas and shoals, and later island archipelagoes. The locations of the morphological elements were mostly controlled by positive structures. The stretching narrow zone of shoals functioned as a barrier and was controlled by large linear tectonic disruptions of the basement and the sedimentary cover, which determined the position of the western and northern ledges of the Caspian syncline. In the tectonically lifted zone, the local structures, and especially those with buried Asselian-Sakmar and Arta reefs and bioherms, contained lowland islands separated by shallow straits, which together formed a long barrier archipelago. These paleogeographic elements became more distinct in the second half of the Elton time. Their influence on lateral differentiation of sedimentation was intensified by the overall shallowing of the sea. It was during the late Elton time that chloride-potassium and chloride-magnesium sedimentation reached a peak; the areas of development of these sediments in this period of the Kungur time (whether determined definitively by factual material or hypothesized from the contours of the main tectonic structures) were the main criterion for drawing the contours of the aquatoria.

Five subbasins of potassium sedimentation can be determined with confidence (Fig. 5):

- Buzuluk subbasin, controlled by the Bazuluk depression (north of Uralsk);
- Utvino-Ilelsk, controlled by Utvino-Ilelsk trough; this subbasin stretched to the north beyond this trough, past the side ledge of the Caspian syncline (a territory in the basin of the middle reaches of the Ural River, stretching sublatitudinally and submeridionally in the east);
- the lower Volga subbasin; its position was determined by the depressions of the seafloor within Krasnokutsk-Ozinkov northwestern trough, Novouzensk trough (Saratov trans-Volga region), southeastern lowest zone of the Volga homocline (Volgograd right bank), Volga region Volgograd trans-Volga region), Sarpinsk trough, and Karasalsk monocline (southwestern part of the lower Volga region), and between the Aralsor uplifted zone in the northeast and Astrakhan arch rise in the southwest (Astrakhan trans-Volga region);
- Chelkar-Indersk subbasin (the basin of the middle and lower reaches of the Ural River), which was controlled in the north by Chelkar depression, and in the central part by Inder depression; it stretched to the southwest from the latter, toward Kamysh-Samara lower zone;
- cis-Mugodzhary subbasin (the area between Emba and Ural Rivers on the right bank of the Ural), controlled by the foredeep, which was the southern continuation of the cis-Ural trough.

These subbasins were partially, but not completely, isolated from one another (at least until the end of the Elton time) by island archipelagoes—Aralsor archipelago within the Aralsor uplifted zone, and Khobda island range formed within Khobda subsided zone. Judging by the absence of potassium salts in this zone, it experienced inversion by the beginning of the Kungur time, and was a positive form in the seafloor relief. The barrier archipelago of the

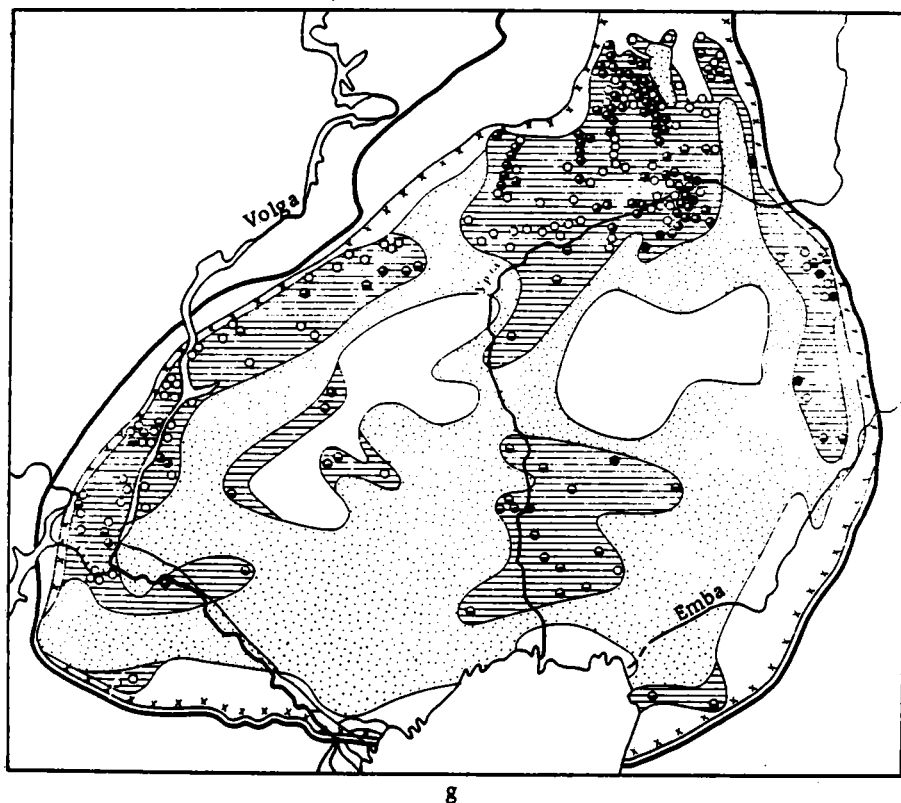
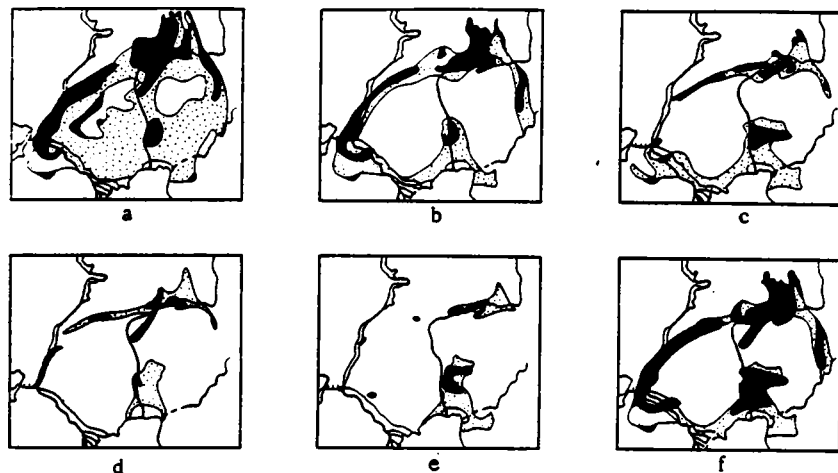


Fig. 4. Polyhalite and polyhalite-containing rocks in Ural-Volga and North Caspian territories. Notations as in Fig. 1.

side ledge of Caspian syncline was an important wall stretching along the western, northwestern, and northern margins of the terminal basin; the islands of this archipelago formed a long chain, and were separated by shallow straits. This archipelago was responsible for isolation of Buzuluk subbasin from lower Volga, and Utvino-Ilel'sk subbasins, as well as substantial isolation of the northwestern zone of the lower Volga basin from its main water body (this zone went beyond the side of the basin). The subbasins, which together formed an integrated system of interconnected elements, despite their partial isolation, were connected either by straits (Buzuluk with lower Volga, Utvino-Ilel'sk with Chelkar-Inder) or by broad shoal zones (Chelkar-Inder with cis-Mugodzhary and Lower Volga basins). These connecting portions were channels for compensational overflows of brine between the subbasins.

There were two additional smaller subbasins of potassium sedimentation. One, the Salmysh basin, was situated in the north within the Salmysh syncline (in the southwestern Bashkiria, near Sterlibashev); the other, Aktyubinsk basin, in the extreme east-northeast area, occupied the Aktyubinsk pericline trough (a meridionally stretching territory near Aktyubinsk).

It is also possible that a small independent subbasin existed between Utvino-Ileksk and Aktyubinsk basins.

Potassium chloride sedimentation in this system of subbasins began as early as the Filippov time, but initially took place only in southwestern subbasins on a small scale and locally (the Nikolaev reference boreholes drilled in Volga homocline have indicated in the Filippov horizon some signs of carnallite, while in the Inder depression at Inder, sylvite and carnallite have been found). In the early Irensk time, the lower Volga (Elton), Chelkar-Inder (Barkhan-nyi, Inder), and cis-Mugodzhary (Shubarkuduk) subbasins accumulated periodically small amounts of sylvite (in Inder they were relatively large).

Sylvite deposition was considerable, and covered large areas in the Ulagan time (see Fig. 1a), especially toward its end. It occurred mostly in the deep parts of large subbasins—Chelkar-Inder (in Chelkar and Inder depressions) and lower Volga subbasin; it was less pronounced in Utvino-Ileksk, and probably took place to some extent also in the cis-Mugodzhary basin. Carnallite accumulated in approximately the same areas (in comparable amounts) (see Fig. 2a). Potassium chloride sedimentation did not take place in the Ulagan time in the Buzuluk basin, which is the northernmost of the system, and closest to the preparatory basin.

The peak of potassium chloride salt sedimentation was the Elton time, especially its latter half. The deposition of sylvite grew in magnitude cyclically (see Fig. 1b-f), was located at that time almost entirely in the tanks controlled by troughs and depressions. The carnallite accumulation area (see Fig. 2b-f), which mainly was also deposited in these tanks, gradually expanded and, in the last third of the Elton time, sometimes occurred on territories outside the areas of relatively stable potassium sedimentation. The magnitude of carnallite sedimentation in these territories, however, was not large.

An important event in the second half of the Elton time was bischofite sedimentation (see Fig. 3), which had previously been local and sporadic (in Ulagan layers at Elton, carnallite rock beds with bischofite admixture have been found; in cycle III at Ozinki a bed of halite-bischofite rock with minor carnallite, apparently in cycle III in the extreme southwest of Karasal monocline and a bed of bischofite rock in Stepnov salt structure). Large amounts of bischofite formations observed in cycles IV and V accumulated at that time. Two aspects were characteristic: 1) bischofite was deposited only in subbasins (in deeper portions) distant from the strait connecting the Caspian terminal basin with Moscow preparatory basin—in cis-Mugodzhary, Chelkar-Inder (exclusively within Chelkar and Inder depressions), and lower Volga basins; 2) the magnitude of bischofite sedimentation increased drastically in the southwestern direction with the distance from the above-mentioned strait. While in cycles IV and V only scattered bischofite mineralization is observed within the foredeep at the eastern margin of the Caspian syncline, these cycles in Chelkar and Inder depressions contain thick lenses of bischofite and bischofite-bearing rocks (especially in Inder). Within Krasnokutsk-Ozinki, Volga, and Sarpinsk troughs, similar lenses of these rocks have been found in many salt structures; in the southeastern slope of the Volga homocline, immediately after the wall ledge of the syncline, thick beds of bischofite and carnallite-bischofite rocks, stretching over hundreds of kilometers (especially in the southwest), have been described.

The final and third outburst of bischofite sedimentation occurred shortly before the end of the Elton time during the accumulation of the upper portion of cycle VI; it was manifested not only at the center of the Chelkar-Inder subbasin (with a few bischofite and carnallite-bischofite lenses in Inder), but also in the southeast of lower Volga subbasin (bischofite lenses in Elton), and in its extreme east-west (thick sylvite-carnallite-bischofite zone in Stepnov salt structure).

All these facts indicate clearly that during the late Irensk time, huge masses of highly concentrated brine were accumulated in the potassium sedimentation subbasins of the Caspian terminal basin, which were the farthest from the northern strait (that connected this basin with the preparatory water body that was the source of salt-rich seawater), and from the eastern shore (the location of folded structures of the south Ural and Mugodzhary, which were the source of fresh continental water flows into the terminal basin). The halogenesis in these subbasins could therefore achieve the extreme eutonic stage, and this indeed happened three times. As a result, large amounts of potassium chloride salts and bischofite were deposited in these subbasins, especially in the lower Volga. Remarkably, the large Elton and Gremyachin potassium deposits with sylvinitic ores with a unique content of potassium chloride developed precisely in the southwest of the lower Volga subbasin (the content of potassium chloride in the commercial beds of Elton deposit is on average 49%; in Gremyachin it is 40%); in the Elton area these deposits are confined to Ulagan layers, and in Gremyachin to cycle IV.

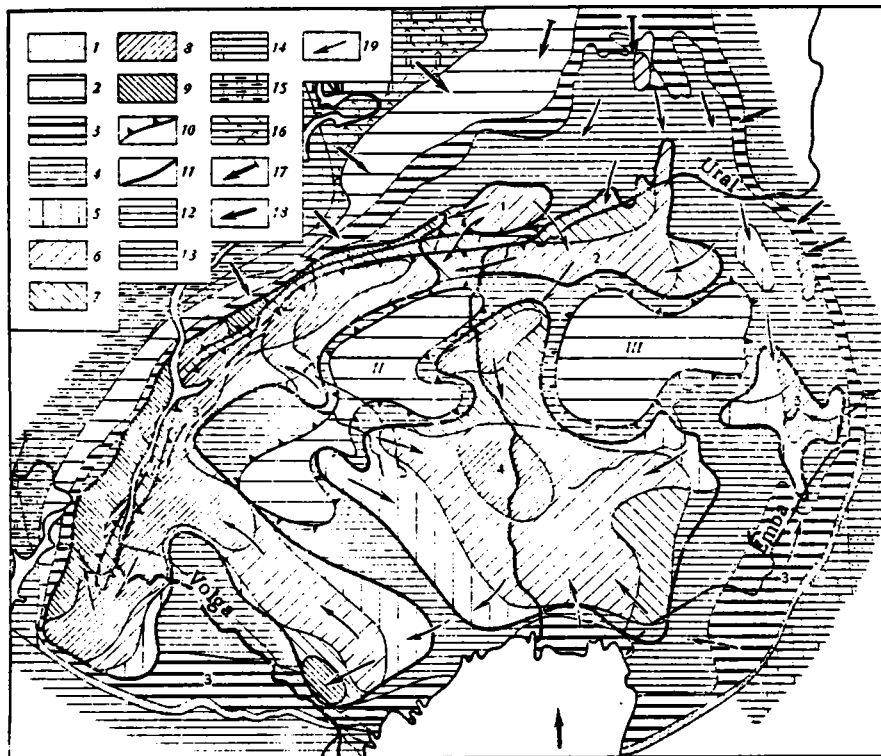


Fig. 5. Paleogeographic schematic map of Ural-Volga and North Caspian region (P_{1kg} Late Irensk time): 1-9) sea areas of predominant sedimentation (1 - terrigenous, sporadic carbonaceous, and sulfate-calcium, 2 - sulfate-calcium, sporadic carbonate, 3 - halite, 4 - halite with occasional precipitation of small amounts of carnallite, 5 - halite with occasional precipitation of small amounts of sylvite and carnallite, 6 - halite with occasional fallout of sylvite and larger amount of carnallite 7 - halite with occasional fallout of larger quantities of carnallite, 8 - halite with occasional fallout of large quantities of sylvite and carnallite, and also large amounts of bischofite, 9 - halite with occasional deposition of large quantities of carnallite and large bischofite masses); 10-11) boundaries (10 - archipelagoes, 11 - main subbasins of potassium sedimentation); 12-13) mountains, drylands with Paleozoic complexes exposed on the surfaces (12 - terrigenous, 13 - carbonaceous); 14-16) plainland with Paleozoic complexes exposed on the surface (14 - terrigenous-carbonate, 15 - clay-carbonate, 16 - sulfate carbonate); 17-18) main directions of influx into Caspian terminal basin (17 - seawater, 18 - continental water); 19) main directions of brine migration in the system of potassium sedimentation subbasins: I-III) archipelagoes (I - barrier archipelago of the side ledge of Caspian syncline, II - Aralsor, III - Khobda); 1-5) subbasins (1 - Buzulik, 2 - Utvino-Ilek, 3 - lower Volga, 4 - Chelkar-Inder, 5 - cis-Mugodzhary).

In Chelkar and Inderbor layers, potassium chloride mineralization is poor; it is found only in isolated salt structures situated in areas which previously, during the Elton time, were occupied by the Chelkar-Inder and the lower Volga subbasins. In particular, in Chelkar strata, sylvite has been found in the salt structures at Zhamaninder, Inder, Makat, and Khar-kin I (Inder depression and associated territories), Baskunchak (the territory between Aralsor raised zone and Astrakhan arch rise), and Stupen (Volga trough); lenses of carnallite rocks or signs of carnallite in the salt structures of Chelkar (Chelkar depression), carnallite signs in Ershov, Karpenkov, and South Ershov structures (the northern side of Krasnokutsk-Ozinkovki trough), and Aksarai (at the eastern extremity of Astrakhan rise). In the Inderbor layers, the sylvinite lenses have been determined in Chelkar and Inder structures; sylvite signs have been found in Zhamaninder structure, and carnallite signs have been observed in Chelkar and Inder structures (i.e., chloride potassium mineralization is present in these layers only in Chelkar and Inder depressions).

These facts show that at the boundary of Élton and Chelkar time, large expanses in the region became dry land. Relatively small Buzuluk, Utvino-Ileksk, and cis-Mugodzhary subbasins of potassium sedimentation disappeared, while the larger Chelkar-Inder and lower Volga subbasins were broken down into semi-isolated and isolated lagoons. Halogenesis in these lagoons followed largely the "dry lake" pattern: it was fed by intercrystalline brine flowing here from loosely lithified salt beds raised over large areas close to and in some locations, even above the day surface. The connection of these lagoons with a northern preparatory basin, however, was not lost completely. This is indicated by the cyclic structure of the Chelkar and Inderbor profiles, and the presence of consistent beds and thick members of anhydrites in them, evidencing periodic flow of new portions of water from the preparation basin into the lagoons.

The stratigraphic associations, quantitative development, and lateral distribution of polyhalite rocks are criteria for determining: 1) the time and duration of the existence of main sources of supply of seawater and hypergenetic continental waters into the terminal basin, which supplied sulfate ions, calcium, and magnesium, as components to form polyhalite; 2) the importance of these sources; and 3) their locations. The information on the occurrence of these rocks in the narrow stratigraphic intervals of the upper Irensk subhorizon and the entire subhorizon (see Fig. 4) clearly points to the important role these components, brought into the terminal basin from outside, and combined with the similar substances in local brine played in the processes and the scale of polyhalite formation. The data of Fig. 4 indicate that during the late Irensk time, three continental sources of supply of these components existed, as well as a marine source (the Moscow preparatory basin).

1. South Ural Source. This source apparently was supported by powerful rivers in the South Urals, which eroded the folded structures and emptied into the basin.

2. Volga Source. In the Irensk time, the northwestern Volga homocline and the southeastern slope of Zhiguli-Pugachev arch contained sulfate-carbonate lower Permian rocks, exposed to the surface, weathered, and partly carsted (Assel-Sakmar and Arta-Fillipov). The products of weathering formed on the surface of these beds, as dust of carbonate and gypsum, were spread around by winds, and in large amounts transported into the water of the terminal basin; the atmospheric waters brought into the beds as an underground flow were saturated with sulfate ions, calcium, and magnesium, and supplied into the litoral zone of the basin.

3. North Caspian Source. For lack of factual data, it is difficult at the moment to determine its nature. It is probable that in the area of North Caspian arch, rivers flowing down from mountain structures of the southern margin of Caspian syncline emptied into the basin, bringing the necessary ingredients for polyhalite formation.

Among continental sources, South Ural was the most important supplier of products necessary, along with potassium, for polyhalite formation. The bulk of polyhalite resources of Caspian potassium basin are currently concentrated in the upper Irensk bed in the northeastern part of the region (Ural area near Orenburg). This was largely due to the fact that these were the only areas where the influence of the marine source of brine was important; this brine, originating from the preparatory basin, was not fully devoid of sulfate, and still contained large amounts of calcium and magnesium. The aeolian transport of carbonate and gypsum dust was responsible for the polyhalite mineralization, observed today, although sometimes on a small scale, throughout the potassium beds of Arta-Kungur halogenic formation.

The sources of continental water gradually weakened during the Kungur age, as the climate became more arid. This affected most the Volga source, which supplied water from the plain-land desert continent, while the other two, mountain, sources were less affected. Decreased scale of polyhalite mineralization in the tip cycles of Élton layers in the north of the region is due also to the progressive shallowing and closure of the straits linking the terminal basin with the preparatory one.

In addition to the main sources, two secondary sources of supply of ingredients for polyhalite into the terminal basin can be distinguished. Apparently, these were Aralsor and Kho Khobda archipelagoes, the which, during the course of Kungur time, increasingly large areas were exposed of the bottom part of Irensk, and then Filippov, horizon, and probably also the older lower Permian sediments, which contained accumulations of calcium sulfate and dolomite (with increasing amounts down the section).

The paleogeography of the region during Kungur potassium accumulation time determined the hydrologic regime of the Caspian terminal basin and its component subbasins of potassium

sedimentation; its action was combined with the climatic factor responsible for intense evaporation. These two factors controlled the general trends of regional compensational flow to the southwest; the paleogeographic factor, in addition, determined the local directions of the compensational brine flows among the subbasins (see Fig. 5). As a result, increasingly large quantities of dissolved components were moved into the southwestern extremity of the terminal basin; this concerned particularly the components which, when crystallized, formed salts falling into the precipitate at the final eutonic stages of halogenesis. These processes were responsible for the concentration of the bulk of sylvinite, carnallite, and bischofite rocks currently found in high concentrations in the southwestern Caspian potassium basin.

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MICROTRANSFORMATIONS OF VARIOUS LITHOGENETIC TYPES OF SANDSTONES

BY HIGH PORE PRESSURES

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UDC 552.51:552.14

In this article we generalized the results of experimental investigation into the effects of anomalously high pore pressures on the deformationally stable and reservoir properties of various lithogenetic types of sandstones under conditions of a nonuniform volumetrically stressed state, as illustrated by the southwestern part of the Donets coal basin. On the basis of microscopic study of thin sections, quantitative microanalyses, scanning electron photographs, and x-ray structural analysis, differences in the mechanisms of remnant deformation in emission-risk and nonemission-risk sandstones were discovered.

Fundamental changes of reservoir, insulating, and physical-mechanical properties are due to microstructural-textural features of catagenically transformed, consolidated sedimentary rocks under the influences of thermodynamic conditions at great depths. It is well understood that increase of depth is accompanied by growth of rock and layer pressures, gas generation, powder formation, and increased temperature. In addition, along with coal and gas emissions, at 700-m depth, rock emissions occur which presuppose the presence of anomalous high pore pressures (AHPP) in the region. To a significant degree, all of these occurrences reduce work safety, retard mine construction, and increase the cost of cutting through preparatory work.

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TABLE 1. Lithologic-Mineralogical Characteristics of Sandstones of the C₂ Suite, Layer h₄¹ of Middle Carboniferous

Sand-stone type	Mineral composition of terrigenous material, %					Cement and its real composition, %					
	quartz	feldspars	rock fragments		mica	total contents	clay (illite)	clay-mica (+sericite-chlorite)	regenerated quartz	carbonate	
			total contents	composition						siderite	calcite
Ia	50—55	20—30	20—25	Silica, clay-silica, quartzic	1—5	10—15	5—15	2—10	3	8—10	2—3
Ib	50—70	20—30	20—30	Clay-mica, clay-silica, seldom silica and quartzic	1—5	10—15	to 5	2—20	1—10	3—10	2—5
II	50—60	20—25	20—25	Clay-mica, clay-silica	1—2	20—35	to 10	to 10	—	15—35	2—5
III	40—55	20—30	10—30	Silica, clay-silica, seldom quartzic	1—2	30—45	to 3	—	—	to 5	30—45

TABLE 2. Physical Mechanical Properties of Original Samples (sandstones)

Sandstone cement	$K_p, \%$	$p_s, N/mm^2$	$p_0, N/mm^2$	$E \cdot 10^{-4}, MPa$	K	$v_L, km/s$	
						along compression axis	across compression axis
Clay-mica	6,28—9,0	89,2—136,1	52,0—93,9	1,19—1,76	1,35—1,51	3,08—4,46	1,8—3,8
Clay-sideritic	9,8—12,0	71,6—82,8	49,4—54,1	0,94—1,25	1,53—1,8	2,9—3,2	2,3—2,5
Calcite	1,8—6,7	121,7—147,0	66,0—70,6	1,31—1,65	1,59—2,2	3,2—5,12	2,12—4,95

In connection with this, we present a determination of the effect of nonuniform volumetric compression and high pore pressures on deformationally stable and reservoir properties and we establish the characteristic features of remnant rock deformations, and rules for their transformations.

The investigated sedimentary sequence of the carboniferous middle is represented by a complex of terrigenous rocks — sandstones, siltstones, and argillites, interbedded with thin layers of limestones and coals. Sandstones form 32–34% of the basic coal-bearing suite C_2^3 of the Donets-Makeevsk region. The object of the investigation were sandstones of this suite, layer $h_4^{1Sh_7}$, of the Skochinsk mine, from the western shaft of the ventilated drift. Three lithogenetic varieties of polymict sandstones were distinguished on the basis of differences in composition, quantity, and cement type:

I) those with clay-mica and hydromica-chlorite cement of the pore, contact, and less often film types; in places in these rocks quartzite-appearing structures are observed, that is, there is growth of contact quartz cement or noncement connection of quartz grains on secondary contacts;

II) those with clay-siderite cement of the contact-pore type, and less often film and basal-pore types;

III) those with calcite cement of the basal and basal-pore types.

Based on the composition of their rock forming components, all three sandstone types are feldspar-quartzitic with the addition of rock fragments and allogenic micas. The basic petrographic features of the selected types are generalized in Table 1. In Table 2, we show data on the determination of open porosity ($K_p, \%$), velocities of elastic longitudinal waves in two directions — along and across layering ($v_L, km/sec$), and the results of tests on the selected rock types by the stamp indentation method in the UMGP-3 apparatus [4]. From the obtained "deformation-loading" diagrams, the following parameters were determined: hardness of the stamp (p_s), yield point (p_0), Young's modulus (E), and the coefficient of plasticity (K). The open porosity was determined by Preobrazhenskii's method. Measurement of velocities of longitudinal elastic waves was conducted by the ultrasonic impulse method at a frequency of 600 kHz.

The results of tests on rocks by the stamp indentation method and the deformation curves indicate the different character of failure and various deformationally stable properties in the investigated rocks. It is recognized that sandstones with clay cement (type I) are elastobrittle rocks with a limited capacity for plastic deformations. Sandstones with clay-sideritic cement (type II) are more plastic, having lower strength and higher porosity. Sandstones with calcite cement (type III) are characterized by high plasticity and large resistance to failure.

Deformational behavior in the above indicated sandstones was studied for a nonuniform volumetrically stressed state which was created by hydrostatic uniform pressure, independent longitudinal loading, and equal pore pressures. A series of tests was conducted on high pressure equipment [3], on cylindrical samples 80 mm in length and 30 mm in diameter, by hydrostatic pressures (σ_2) of 50 and 100 MPa and pore pressures (p_p) of 15, 25, 40, 50, and 75 MPa. The pore pressure was created by distilled water.

In the investigated pressure range, the samples failed along cleavage planes which had angles of 20–30° (for small pore pressures) and 25–40° (for pore pressures of 50–75 MPa) with longitudinal loading. The cleavage surface, in spite of the complicated mineral composition of the rocks, was uniform and smooth with a film of finely ground mealy material of white color.

TABLE 3. Parameters of Microfracturing in Various Lithologic Types of Sandstones, Original and Deformed by Different Pore Pressures

Sandstone type	Test conditions		T_{mT} l. m	m_T %	$K_T \cdot 10^6, \mu^2$	T_0 l/m
	σ , MPa	p , MPa				
I	Original		—	0,01	1,0	5—10
	50	0	—	0,03	1,2—1,4	15—18
	50	15	—	0,01	0,3—1,0	5—10
	50	25	—	0,02	0,3—1,2	5—10
	50	40	—	0,03	1,3—1,7	18—20
	100	50	—	0,037	2,5	20—25
II	100	75	20—30	0,04	3,1—3,8	35—40
	50	25	—	0,018	1,2	10—15
	50	40	—	0,018	1,1—1,5	15—18
	100	50	—	0,02	1,3—1,8	15—18
	100	75	50—80	0,025	1,5—1,2	18—20
	Original		—	0,01	1,0	10—12
III	50	15	—	0,01	1,0—1,3	10—12
	50	25	—	0,01	0,8—1,1	10—15
	100	75	80—100	0,017	1,2	15

As the conducted experiments showed, for a single hydrostatic pressure with growth of the pore pressure, all of the tested varieties decrease in strength and display a maximum capacity for deformation. This phenomenon is explained by the chemical reaction, solution, and physical absorption of material on the solid surface, which cause a decrease in the free energy of the tested material, and as a consequence, facilitates the process of failure and plastic deformation. In the process of deformation, all of the samples displayed a capacity for uncompaction. The absolute magnitudes of void growth increase with growth of P_p (for identical hydrostatic compression), that is, the process of fracture formation is intensified. The exhibited feature of deformational behavior in sandstones - volume change - presents the greatest interest. The most significant microstructural-textural changes of sandstones are noted at hydrostatic compression of 100 MPa and pore pressure of 75 MPa. The magnitude of volume growth in the sandstones of types I, II, and III comes to 0.7-1.75, 0.4-1.14, and 0.3-0.5%, respectively.

For explanation of the effect of uncompaction as well as samples of deformed microtransformations which accompany remnant rock deformation, we used the following complex of methods: comparative analysis of thin sections of original and deformed samples with computation of their fracture parameters by the VNIGRI method [2], quantitative microanalysis with the aid of a system consisting of an electron microscope (REM) Geol, JSM-50A, a connected image analyzer (IA) and a DEC PDP-8 minicomputer [5]. In addition, natural oriented cleavages in the original samples were photographed, both before and after the test at magnifications from 300 to 30,000. With the aid of the microscope (REM), we investigated the morphology of the samples' cleavage surfaces after testing along and perpendicular to the surface of the main cleavage of each sample.

Qualitative changes were shown by comparative petrostructural analysis of data on rock microfracturing over the course of the experiment which modeled the thermodynamic natural effects. The width and length of openings and mineral intra- and intergrain fractures increased with the growth of pore pressure under conditions of nonuniform volumetric compression. As a result of these phenomena, such fracture parameters as volume density of opening (T_0) and mineral (T_m) fractures, fracture porosity (m_T) and permeability (K_T) grow in the deformed samples of sandstones (Table 3). The largest changes are noted in sandstones with clay cement; sandstones with calcite cement are altered less.

Experimental data and petrostructural analysis are confirmed by results of quantitative computation of fracture parameters in polished sections. Scanning of polished oriented surfaces of original and deformed samples in two mutually perpendicular directions made it possible to obtain following characteristics of void space: area (A, %), average size of chord (H , μm), specific surface (S , mm^{-1}), form factor (F) and coefficient of orientation (K) of pores and fractures.

From the data shown in Table 4, it follows that the volume A, the average chord size H, and the absolute specific surface S of void space have a higher value in the deformed samples than in the original samples. The decrease in the value of the form factor F with the in-

TABLE 4. Results of Computation of Sample Void Spaces
(for $\sigma_2 = 100$ MPa, $P_p = 75$ MPa)

Sandstone type	A, %	H, μm	S, mm^{-1}	F	K
I	7,99	13,83	21,1	0,063	1,19
	13,99	16,17	38,47	0,047	1,079
II	8,04	12,9	24,6	0,052	1,077
	12,79	14,52	32,84	0,043	1,078
III	3,21	9,37	12,28	0,067	1,15
	4,95	11,7	17,0	0,059	1,042

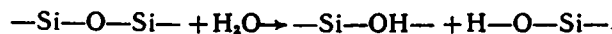
Note. Data for the original samples are shown in the numerator, and for the deformed samples in the denominator.

crease of the specific surface indicates an appearance of fine separate pores and fractures of complex configuration in the volume of the deformed sample. The orientedness of the void space in sandstones varies insignificantly.

Thus, the methods described above first of all confirmed the predominance of brittle failure in the deformed samples, with an abundance of fractures of various orientations and sizes. Their intersections often form microbreccia. Vertical cleavages with fractures are characteristic, as well as transverse cleavages with displacements, the knocking-out of individual blocks of minerals, and granulation zones (Fig. 1).

It is necessary to note that we are dealing from the first with intensively transformed, often fractured rocks (see Table 3) [5]. In particular, before deformation, the quartz (which is the principal rock forming mineral of the investigated sandstones) and its regenerated portions, before the deformation already exhibited fractures and undulatory extinction, induced by the block structure and the natural deformation. The majority of grains contain chain inclusions of very fine gas or liquid bubbles, which were formed by the factor of crystal growth. At the time of deformation, the presence of these defects promotes the development of microfractures. Growth of fractures is initiated on such segments, where high P-T parameters create stress concentrations. Actually, these already existing point defects are displaced and create separate groupings, as a result of stress redistribution. Alignment of the gas-liquid inclusions into subparallel chains is observed in the deformed samples. These chains, merging, form fracture type of defects. Slip of separate parts of the crystals relative to one another occurs in some of them.

In addition to brittle failure in the quartz grains, plastic deformation is also noted. This occurs by various processes. If "dry" quartz is brittle material even under conditions of high pressure and temperature, then in the presence of water, in agreement with recent concepts [6], hydrolysis of the strong silica-oxide bond is possible, with the formation of weaker Si-OH:



Hydrolysis facilitates the motion of dislocation as a result of breaking the weak hydrogen bonds, and leads to the formation of readily apparent slip lines. One of the important slip mechanisms in such hydrolytically weakened material may be the distribution of kinks on dislocations in proportion to hydrolysis of adjacent bridging bonds of $-\text{Si}-\text{O}-\text{Si}-$. All of these phenomena enable the dislocations to move because of exchange by weak hydrogen bonds.

Presented below are results obtained from the study of natural cleavages in the original sandstones and in those deformed by lateral hydrostatic pressure σ_2 100 and P_p 75 MPa, since it is namely under these conditions that the most significant microstructural-textural changes are observed.

In electron photographs of the original samples, it is possible to observe both smooth, uniform quartz surfaces, as well as conchoidal fractures and the characteristic thin hemispherical ribbing (Fig. 2a, b, c). Multiple etching figures (defect traces) are observed on the surface of the prism's face, with very short, elongated, somewhat sinuous, deeply furrowed form. All of the etching figures, which uniquely correspond to the emergences of dislocations, are arranged on the face of the crystal in an oriented manner (see Fig. 2).

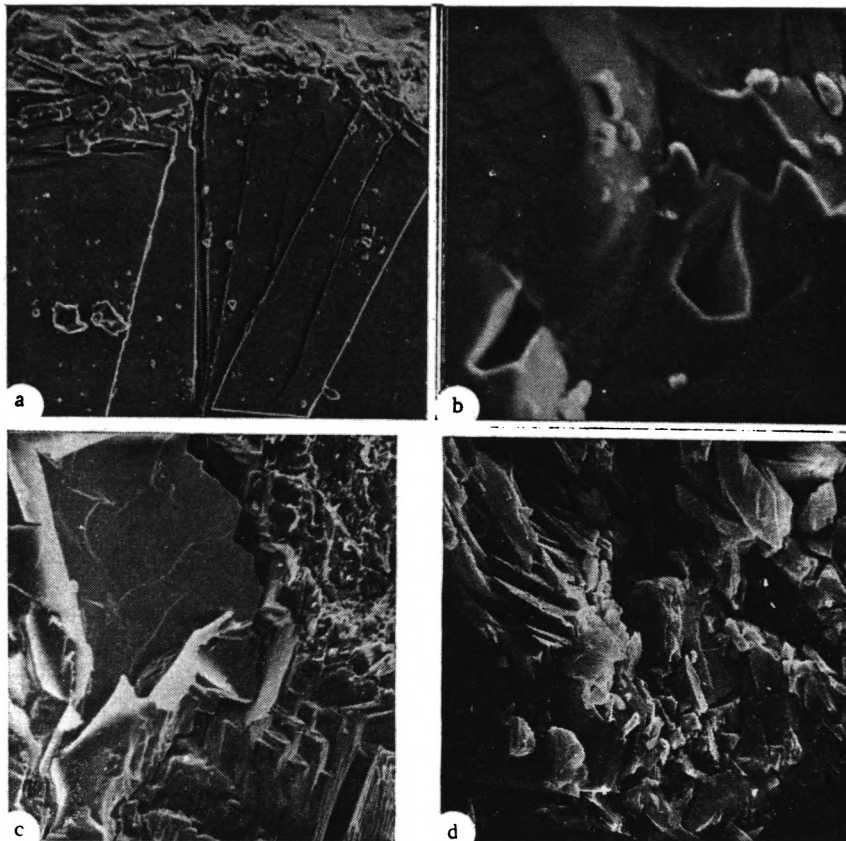


Fig. 1. Types of brittle deformation. Cleaving of a deformed sample, oriented parallel to the load axis. a) Development of fractures along cleavage in calcite, displacement of separate microblocks relative to one another; change of the grain's outer surface: formation around it of finely crushed material, $\times 3000$; b) Voids on the surface of quartz grains - the result of falling out of blocks; sawtoothed cleavages, $\times 4500$; c) Breakage fractures along a rigid quartz and feldspar contact, $\times 4000$; d) Formation of granulation zones, resulting from emergence of fine and thin fragments, often worn and amorphous on the surface, $\times 3000$.

Feathery-stepped structures are observed in the deformed samples on the cleavage surface, which indicate internal twisting motion. Several microsteps are complicated by transverse, sharply defined kinks. The dislocation density reaches high values (see Fig. 2d, e). The slip surface is often split by microfractures, with the formation of fine mineral powders partially amorphosed as a result of the high temperature fusion of material in the process of friction along cleavage surfaces (mirror slip).

Water also shows an analogous plasticizing effect on feldspars, in which are formed, as a result of plastic deformation, kinks of twin seams that are thin in comparison with the original samples, tapering of microblocks along the cleavage planes, formation of right angled and rhombohedral platelets at an angle to them (Fig. 3) [5].

Plastic deformation of the allogenic admixture of micas occurs by means of thin stratification, with the formation of kinks and flexures in the platelets. In the original samples mica is represented principally by platelets of isometric elongated form. In the deformed samples, the biotite laminae have ragged edges with split, bent tips (Fig. 4) [5]. The crumpling of micaceous contaminants (sericite, muscovite and biotite), the extrusion of material along determined textural directions and slip planes into free space, and its redistribution between the grains by the principle of densest packing are all related to the phenomena of plastic deformation.

The process of indentation of single microblocks into one another with the formation of stylolitic boundaries is also related to the phenomena of plastic deformation. The outer surfaces of detrital grains, which are immediately adjacent to one another, undergo deformational transformation in the course of the test. Zones of cataclasis up to 0.02 mm in width

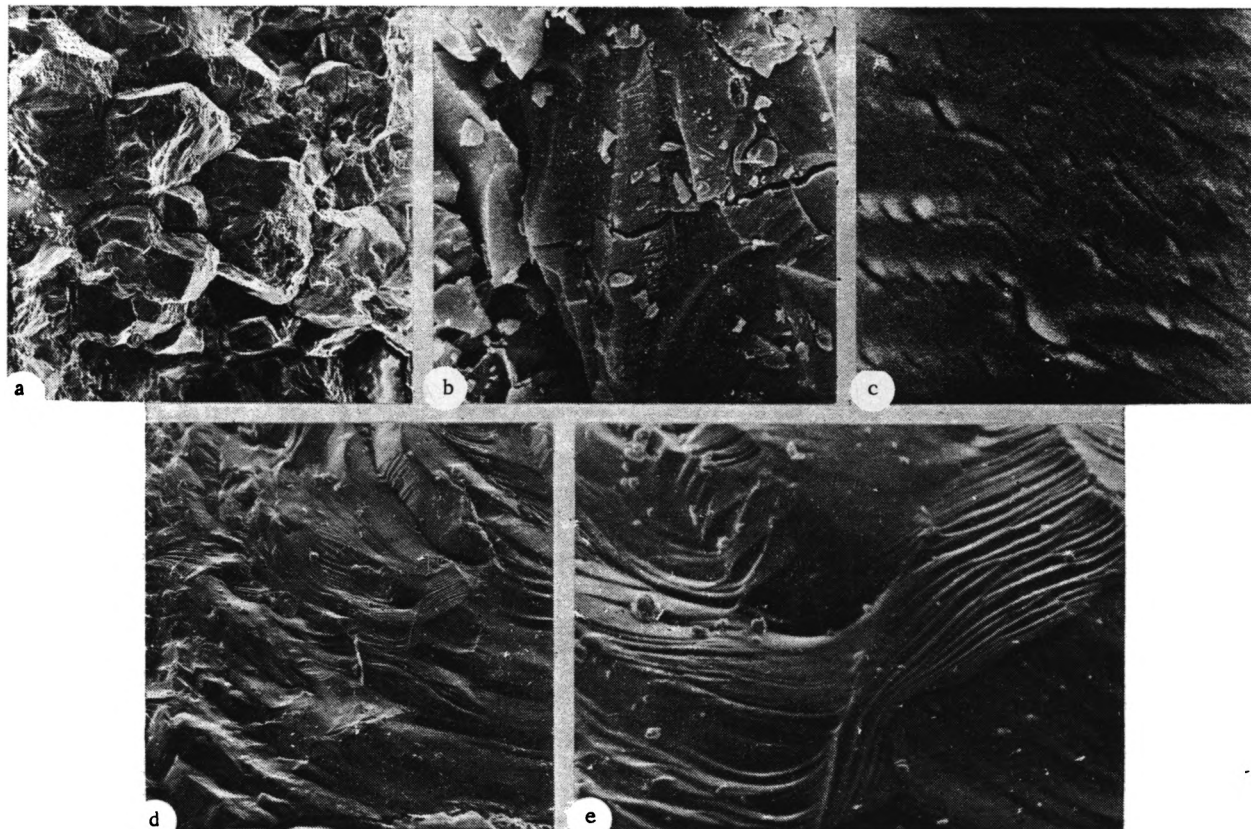


Fig. 2. Morphological features of quartz grains. Cleavage of original (a) and deformed (b-e) samples, oriented parallel to the loading axis. a) Quartzitic appearing structure in a sandstone-rigid intergrowth of grains into one another with the formation of stylolitic seams on the contacts, $\times 1000$; b) quartz surface with conchoidal fracture and characteristic thin, hemispherical ribbing, $\times 1000$; c) oriented distribution of etching figures on a prism face, $\times 30,000$; d, e) feathery-stepped structures are observed on cleavage surfaces, indicating complex turbulent motion, $\times 300$, 1000 , respectively.

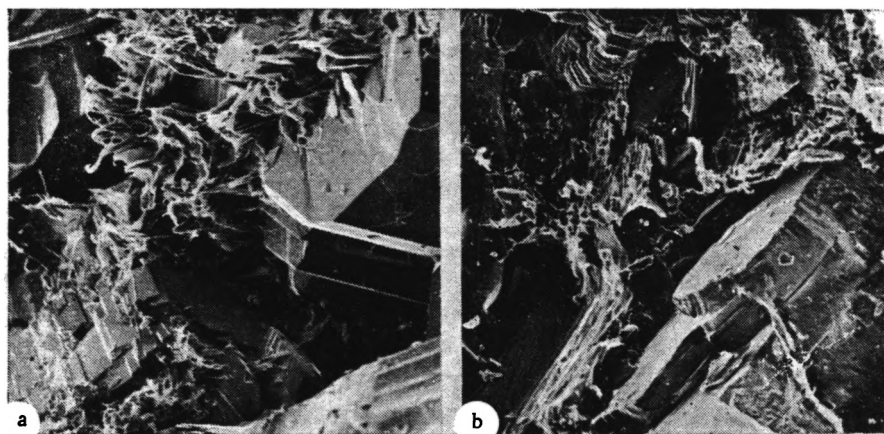


Fig. 3. Morphological features of feldspar grains and the character of their interrelationship with clay cement. Cleavage of original (a) and deformed (b) samples, parallel to the loading axis. a) Detrital feldspar grain in an edging of the clay mass, $\times 500$; b) Feldspar grain in an edging of newly formed kaolinite (the regular hexagonal tabular crystals or intact packets, well crystallized, and clearly laminated with clean basal surface, $\times 3000$).



Fig. 4. Deformational microstructures in micas. Furrows are noted on the basal surface of the bent mica platelet - the sign of directed slip, $\times 3000$.

formed around them, complicated by pelitized material (see Fig. 1a). In this case, the grain itself may be crushed into separate blocks, and microfractures that existed earlier and emerged at the time of deformation, commensurate with the grain's size, are filled by finely crystalline materials of quartz and feldspar composition. Local displacements of separate mineal grains or their parts relative to one another are made possible by plastic deformation (see Fig. 1c, d). All of these described processes may be accompanied by amorphization and recrystallization of material.

On contact with the plastic clay material of the cement, the detrital grains acquire some mobility. They tend to occupy the most stable position, and swing to the direction which is dictated by the maximum compressive stress. Their bond with the clay particles is destroyed by this; isolation of the grains from the cement by fractures and acute-angled fragments occurs.

Qualitative changes also occur in the cement under the influence of anomalously high pore pressures.

Investigation of thin sections and photographs, obtained with the aid of the electron microscope showed that at the time of deformation, three dimensional loose particles of clay minerals of thin sculpture become more dense (Fig. 5). Their expressed orientation in the direction of maximum shearing stresses is clearly observed. The appearance of reorientation, and hence some distortion of the crystalline lattice of clay minerals within the considered pressure range, is confirmed by diffractograms, in which a decrease in the reflection intensity of 2-4 times is noted. Through this, the crystalline structure of the clay minerals is preserved.

Slip of the fragmental portion of the rock is possible along the forming weakened zones, which thus creates grain-orientation of the deformed sample. Such reorientation is facilitated by the formation and growth of intergrain fractures in the direction of longitudinal compression.

Significant changes are also observed in the calcite cement. The presence of water insignificantly lowers the surface energy of the calcite, and this, along with the possible diffusion of surface defects eases the motion of dislocations and their emergence onto the surface. The consequence of these processes is the formation of multiple lines of intra- and intercrystalline slip, the tapering of twin zones, the growth of cleavage, finally, fractures principally on grain boundaries (see Fig. 5f, g).

The cementing mass of the type II sandstones in the original samples is represented by finer grained clay and ferrous carbonate (siderite) material of irregularly clustered and nodular structure. The form of the siderite grains is diverse: from regular subrhomboidal to

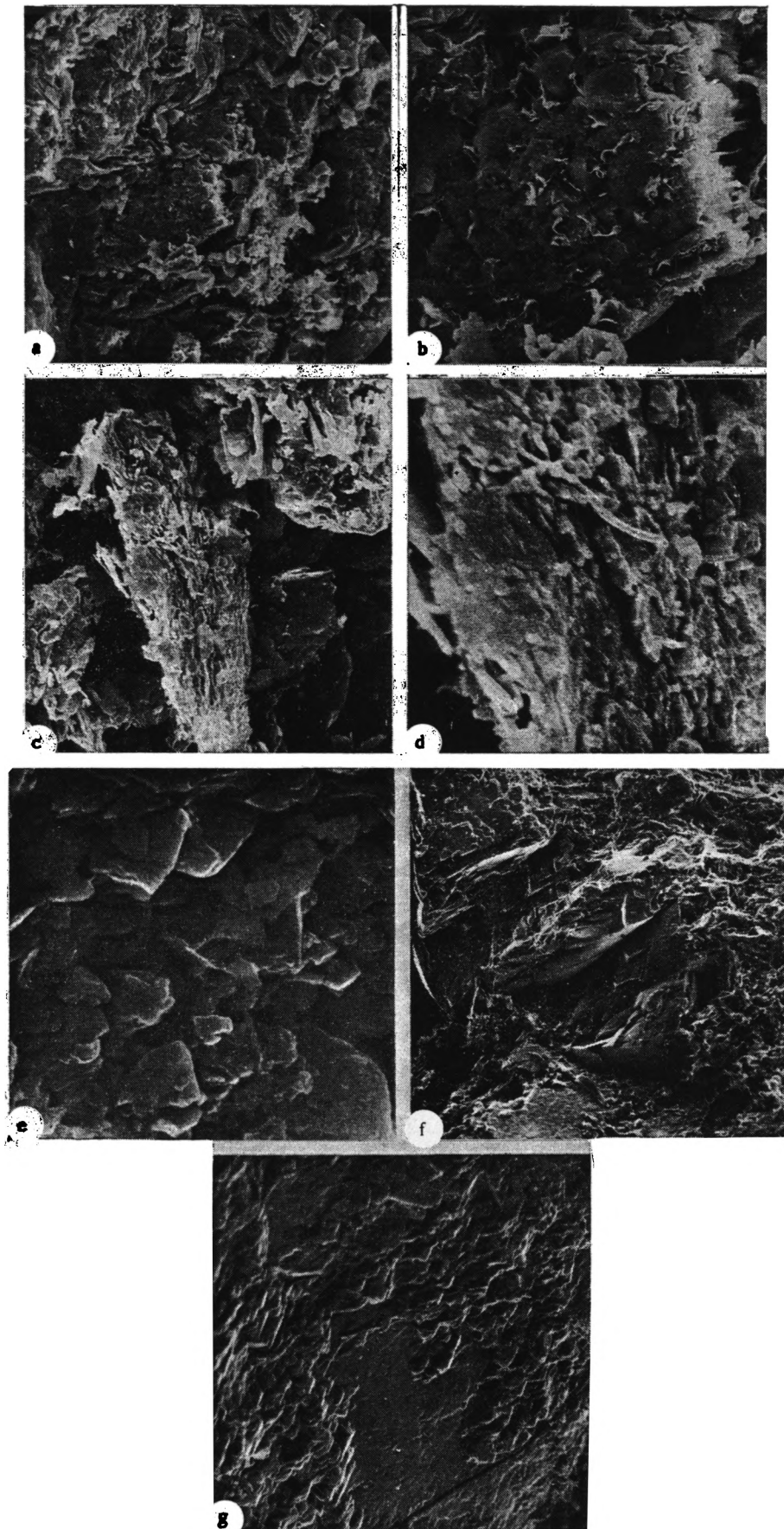


Fig. 5 (a-g)

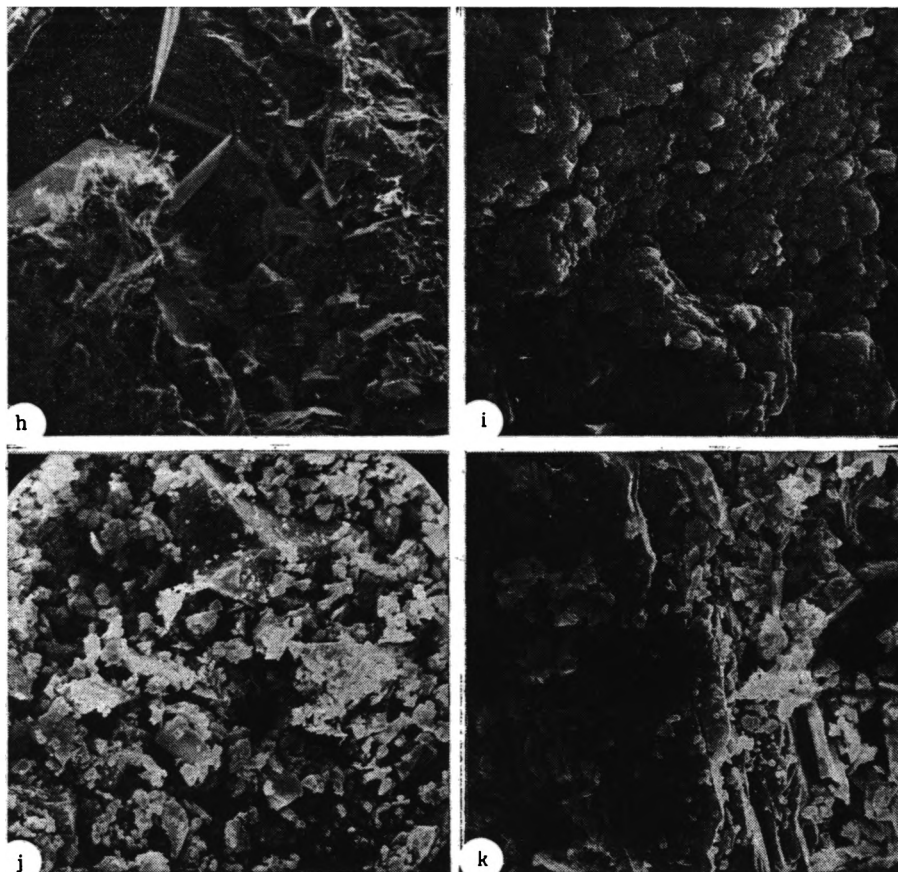


Fig. 5. The character of the clay-mica, calcite, and clay-siderite cementing mass in original (a, b, e, h) and deformed samples (c, d, f, g, i-k). a, b) Clay-mica, hydromica-chlorite cement. Loose, thin particles of fanciful isometric form are characteristic, $\times 1000$, 3000 , respectively; c, d) compaction, orientation, and lamination of clay material, $\times 1000$, 3000 , respectively; e) calcite cement. Crystals with sharp conjunction boundaries are characteristic, $\times 1000$; f) calcite diffusion - the crystal forms are rounded, with soft, smooth outlines, $\times 1000$; g) twinned calcites along two intersecting planes, with the formation of planar slip, $\times 1000$; h) clay-siderite cement. Grains of regular subrhomboidal form are characteristic, $\times 1000$; i) formation of rock lenses by fractures, $\times 2000$; j) loose structure of clay-carbonate material with irregular, palmate form; particle disintegration; $\times 3000$; k) separation of clay-siderite cement and the fragmental portion, with the formation of granulation zones and microfractures along the contact, $\times 3000$.

globular concretions (sphaeroidite) (see Fig. 5h). Under the influence of high pore pressures, the siderite-clay cementation mass is uncompacted as a result of microfracture development along the grain boundaries, or as a consequence of opening of microfractures and formation of rock lenses along them, with formation of pillars between the fractures. As a result of these phenomena, opening of structural-textural defects and the growth of basic fracture parameters occur (see Fig. 5i, j, k).

The morphology of the void space is altered as a result of the deformation. Isometric rounded pores acquire an elongated, slotted form, transitional to fractures.

Thus, the large variety of deformation types on the scale of optic and electron microscopy is explained by the multiple-component composition of the samples, where each mineral, having its own defined physical properties (hardness, plasticity, etc), will conduct itself separately.

The general aspect in the development of remnant deformation is the development of intracrystalline effects.

Remnant deformation of polymict sandstones with clay-mica and clay-chlorite cement is accompanied by reorientation of the cement's clay minerals as a result of rotation, and sometimes kinking of separate mica platelets. Reorientation facilitates the formation and growth of intergrain fractures, their opening and rupture, as a result of which the rock is uncompacted, and the volume of void space and the fracture permeability is increased.

Remnant deformation of polymict sandstones with calcite cement is accompanied by twinning of the calcite cement crystals, and development of intracrystalline fractures along twin junctions and at an angle to them. These fractures uncompact the rock and assist in the growth of its capacitive and filtration potential.

Polymict sandstones with clay-siderite cement are uncompacted as a consequence of the development of intergrain microfractures, particle disintegration, and forming of lenses in the rocks. As a result of these phenomena, opening of textural-structural defects and growth of the basic fracturing parameters occurs. The difference in change of permeability at the time of deformation assists various degrees of degassing.

Uncompaction, accompanying remnant deformation, depends not only on different mechanisms of plastic deformation and the macro- and microstresses connected with them, but also on the structure of the rocks and the degree of their catagenic transformation.

Polymict sandstones with clay-mica cements, and with hydromica-chlorite cements in particular, contain an increased quantity of the most elastic material - quartz. They are characterized by a high extent of contacts between the grains of rock forming minerals. Formation of regenerated quartz, contact and indentation cement, as well as the appearance of microcrystalline quartz in the cement, presupposes the formation of a more rigid skeleton with increased brittleness and high elastic properties, which takes place in these sandstones in natural deposits. High (1-5%) content of hydromica, muscovite, biotite, and secondary sericite in the contact type of cement, in the absence of carbonate, leads to intense disintegration of the rocks. A consequence of this is decreased stability properties in comparison with other types of sandstones in regions with coals in the middle stage of metamorphism.

As reported, in a sandstone which possesses a rigid skeleton, the "framework" of the sandstone is able to accumulate the energy of elastic deformations, through the stresses connected with the pressure of overlying sequences, tectonic processes, gas pressure and the energies of explosive waves etc. Through knowledge of development in the layer of such a sandstone, the presence of void space in the rock massif causes realization of the elastic energy, which is accompanied by destruction and emission of the sandstone.

Sandstones that do not possess a rigid skeleton and that have a significant content of plastic clay material, undergo plastic deformation to a large degree upon the receipt of supplementary energy. There is small probability of the conservation of elastic stresses by these sandstones.

A significant admixture of carbonate (both as siderite and as calcite) in the cement of the types I and II sandstones decreases the disintegrating influences of the micas, which is indicated by an increase in the coefficient of plasticity. Development of calcite in the sandstone cement hinders the formation of a rigid skeleton, which in its turn makes it impossible to reflect on the emission-risk of the sandstones.

In natural conditions, under the action of tectonic stresses and the influence of AHPP in sandstones, oil and gas accumulations may form which are correlated to fracturing zones, and which accumulated fluids. Change in the stressed state of the massif, caused by dynamic loading on the layer, the rapid intrusion of mountain building into the layer, as well as the opening of the layer by explosion, may lead to sudden emission, as was observed in the Skochinsk mine.

Emission occurred in the underwater-delta sandstone, which is correlated to the upper part of the Zaboi. Below the emission-risk layer lies a sandstone which does not take part in the rock emission. Lithologic-petrographic study of these layers indicates a general facies identity, and close petrographic composition. However, along with this, an increased calcite content and the absence of an elastic framework is noted in the lower layer, which also caused its passive relation to emission. This indicates that the calcite content in the cement in quantities up to 8%, independent from the genetic identity and stage of postdiagenetic transformation of sandstones, determines their nonemission-risk [1, 5].

The results of experimental study on the action of nonuniform compression stresses have a practical value, and they should be considered in the prediction of deformational-stability and reservoir properties at great depths.

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PIGMENTATION OF STRATALLY OXIDIZED ROCKS AND ITS SIGNIFICANCE FOR GEOLOGIC RECONNAISSANCE

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UDC 552.14:552.5

The pigmentation of stratally oxidized rocks, which control infiltrational uranium and accessory metallization, is shown to be connected with the lithologic facies features of the environment, the position of the segments in the profile of epigenetic zonality, the alkaline-acid regime of the mineralization medium, and the presence and nature of preceding epigenetic alteration.

Zones of stratal oxidation are an important controlling factor and reconnaissance criterion of stratal-infiltrational uranium metallization (and associated Se, Re, Mo, and other metals) [5, 8, 11, 12, 16, etc.]. The color of stratally oxidized rocks varies from off-white to dull green-yellow and bright yellow-brown or pink-red. It is generally associated with partial or complete replacement of minerals of ferrous iron by hydroxides of Fe(III), caused by the activity of oxygenated pressure waters of artesian basins [11]. The reason for the diversity of color of rocks currently or previously subjected to oxidation are often unclear, and have not been studied sufficiently.

Stratally oxidized rocks exhibit an epigenetic zonality representing the sequence of oxidation of iron-containing minerals [5, 16]. In an oxygen environment the easiest to be destroyed and replaced by Fe(III) hydroxides are authigenic minerals: disulfides of Fe(II)—pyrite and marcasite, and carbonates of Fe(II)—siderite and ankerite. The iron-containing clastic minerals are not as oxidizable: aluminosilicates (chlorite, biotite), hard-to-decay oxides (magnetite), and titanites (ilmenite), and authigenic hydroaluminosilicates (glaucophane) and clay minerals, which include Fe(II). As a result, it is possible to distinguish, according to the fullness of oxidative reactions and preservation of the initial Fe(II)-containing components within the stratally oxidized zone, the following subzones: a) total oxidation (posterior), b) incomplete oxidation (intermediate), and c) partial oxidation (frontal) [16].

Oxidation reactions of easily decaying Fe(II) minerals — involving the substitution of iron hydroxides — occur with release of H-ions, i.e., an acidulation of the medium:

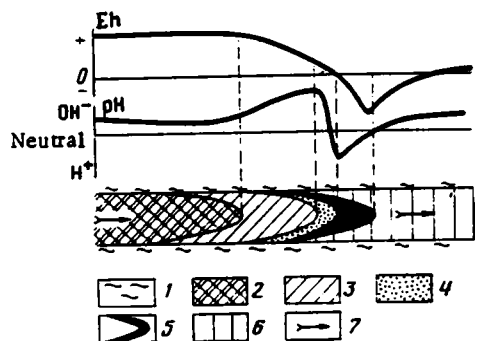
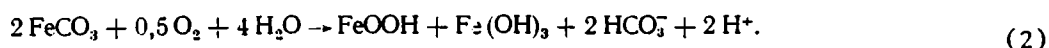
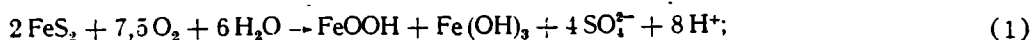
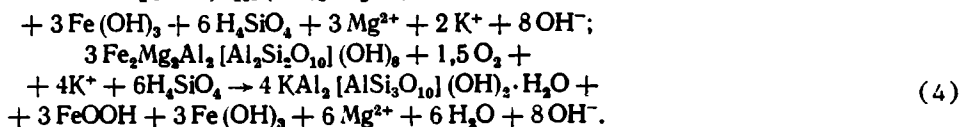
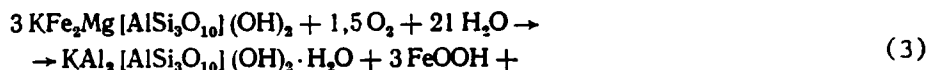


Fig. 1. Zonality of stratally oxidized rocks with Eh and pH variations of the environment: 1) water-resistant rocks; 2-4) stratally oxidized permeable rocks with oxidation subzones (2 - complete, 3 - incomplete, 4 - partial oxidation); 5) uranium metallization zone; 6) unoxidized nonore rocks; 7) direction of stratal waters.



The same effect of a drop in pH takes place also when coaly or bituminous matter is oxidized [8].

The oxidation of more resistant aluminosilicates which, in addition to ferrous iron, contain alkalis and alkaline earth (especially magnesium), is accompanied with the opposite effect - alkalinization of the medium, according, for example, to the reactions of oxidation of biotite and Fe-Mg-chlorite*:



As a result, the stratally oxidized zones developing after rocks with authigenic disulfides of Fe(II), as well as clastic minerals - aluminosilicates, such as biotite or iron-magnesian chloride - would typically exhibit alkaline-acid zonality, observed as a succession of an acid wave at the leading front of the movement of the zone of limonitization, followed by an alkaline wave, which opens the posterior part of this zone. The process is schematized by Fig. 1.

According to the pigmentation, the following types are distinguished among stratally oxidized rocks: 1) brown-yellow, 2) off-white-yellow, 3) white, 4) green-yellow, 5) pink, and 6) yellow-pink.

The brown-yellow types corresponds to the zones of stratal oxidation of rocks with higher presence of authigenic iron minerals (pyrite, marcasite, siderite, ankerite, chamosite, and others), and usually organics. Fe_{tot} concentrations in unaltered rock are higher than 1%. $\text{Fe}(\text{II})_{\text{pyr}}$ is 0.2%. These are mainly sandstones with clay cement, or sands containing clay interlayers, "shreds," and pellets.

Paleogeographically, these rocks are sediments of marine offshore areas and shoals and submerged deltas, alluvial sediments of humid provinces, and sediments of portions of flood valley channels of large transient rivers (at their lower reaches). The terrigenous grains are of a quartzose or quartzose-feldspathic composition with a small presence of mica, silica, and rock fragments. Zones of stratal oxidation are sometimes of a regional scope, and develop

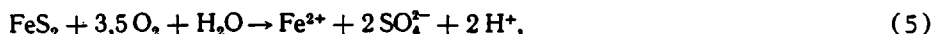
*Influx of K^+ and H_4SiO_4 into reactions (4) is made possible by concentrations of these substances in groundwaters of arid provinces, where they attain 15-20 mg/liter.

from primary red rocks adjacent to infiltration areas. Initially, after polymictic slightly reduced sands of a proluvial-alluvial belt, then after clay-sand deposits of the lower reaches of the valleys of large rivers, the submerged delta and the seashore. The brown-yellow types in this case are limited to the frontal parts of these zones. Toward the rear parts, the pigmentation of the stratally oxidized rocks, in accordance with the facies variations, becomes off-white, yellow, or pink, rather than brown-yellow. These features are observed in particular in the deposits described by the authors in alluvial sandstones [9]. The brown-yellow zone width varies from tens of meters to several kilometers.

The typomorphous minerals of stratally oxidized rocks of this type are goethite and hydrogoethite, which form brown-yellow, yellow-brown, and orange powderlike accumulations and crustlets in the sandstone.

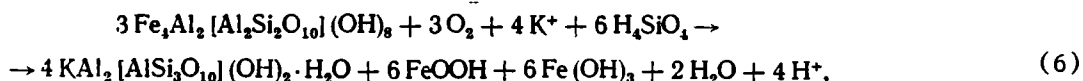
Near the zone where the stratal oxidation wedges out, the segregation of neomorphous hydroxides of Fe(III) usually appears as distinct pseudomorphoses after disulfides and carbonates of Fe(II). In the back portions of the profile of oxidative zonality, a local redistribution of ferric iron and its fixation in disseminated segregations of brown-yellow hydroxides on grains of different minerals is observed; goethite in such cases is replaced by hydrogoethite [16].

The formation of brown-yellow hydroxides of Fe(III) after pyrite and siderite is described by reactions (1)-(2). The acidulation of the medium results in a partial removal of Fe(II) from the frontal portions of stratally oxidized zone, in conformity with the reaction

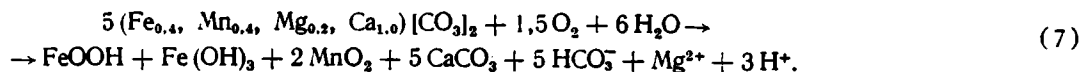


which leads to a lighter pigmentation of rocks and subsequent deposition of epigenetic iron disulfide in the adjacent ore zone [14].

Oxidation of ferruginous chloride (chamosite), which occurs according to the reaction



produces a mix of goethite-hydrogoethite and hydromica; biotite is decayed similarly. The oxidation of manganous-ferruginous carbonates gives rise to an aggregate of hydroxides of Fe(III) and Mn(IV), coloring the rock with black-brown small spots:



The brown-yellow color of rocks from aquifer horizons produced by stratal oxidation of sand-clay varieties rich in reducing materials (iron disulfides and organics) is generally a favorable sign of stratal-infiltrational uranium mineralization and its accessories (Se, Re, and Mo) because it is an indicator of contrastivity of the reduction barrier at the site of the wedging out stratally oxidized zones.

At the same time, this type of stratally oxidized rocks is characterized by active uranium sorption on neomorphous Fe(III) hydroxides. This involves enrichment of these rocks in uranium, as compared with unaltered gray varieties [13]; the latter cannot be a source of useful components in infiltrational metallization. Ore formation therefore requires here additional sources of ore material beyond the facies zones or enclosing horizons, i.e., uranium has to be imported by infiltrational oxidation waters from adjacent regions of occurrence of low-iron sediments or from basement rocks.

Off-white-yellow type is common in the zones of stratal oxidation of sand rocks containing total iron amounts from 0.2 to 0.8%. These concentrations are usual in well-sorted feldspar-quartz and oligomictic quartz sands, which are estuarine sediments of large valleys of ancient rivers, and sometimes littoral and shallow-sea sediments. The stratally oxidized sands display even or speckled light yellow pigmentation with points of Fe(III) hydroxides after pyrite-containing rock fragments, minerals of the heavy fraction, and pyrite-containing coaly detritus. Terrigenous matter (quartz and feldspars) and clay cement have pale yellow pigmentation. Distinct pseudomorphoses of Fe(III) hydroxides fix the contacts with interlayers and pellets of clays and sporadic sediments rich in Fe(II) disulfides and coaly matter.

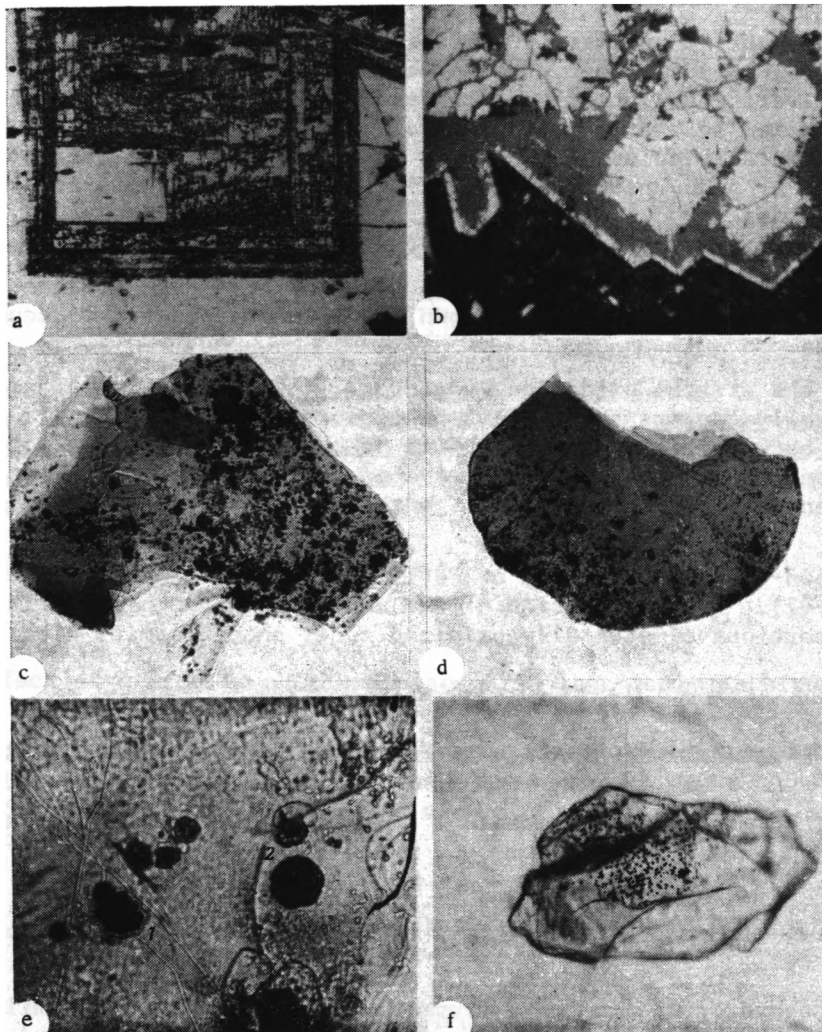


Fig. 2. Iron oxides and hydroxides in stratal oxidation zone, Upper Senonian (a-c - yellow rocks, d-f - pink rocks): a) initial stage of pyrite substitution by goethite in growth zones, reflected light, magn. $\times 1000$; b) partial goethite pseudomorphosis after pyrite, reflected light, magn. $\times 400$; c) globular rusty brown goethite aggregates in clastic biotite, transmitted light, magn. $\times 320$; d) globular red hematite aggregates in clastic biotite, transmitted light, magn. $\times 320$; e) partial (1) and complete (2) red hematite pseudomorphosis after pyrite in clastic biotite, transmitted light, magn. $\times 500$; f) globular red hematite aggregates appearing as dust on clastic grains, transmitted light, magn. $\times 200$.

Like in brown-yellow rocks, goethite pseudomorphoses of a yellow, rusty brown, and orange color are formed after pyrites of all morphological varieties (Fig. 2a, b). Pseudomorphoses replacing large pyrite-marcasite concretions are accompanied by partial redistribution of iron with formation of lixiviation cavities within the nodules and collomorphous aggregates of Fe(III) hydroxides in the enclosing sands. In clastic biotite, globular aggregates of rusty brown goethite are formed (see Fig. 2c).

Off-white-yellow stratal oxidation zones in thick beds of monotonic low-iron alluvial sands, low in reducers, are not normally associated with practically significant infiltrational uranium metallization. The latter is formed only at conjugations of the areas where the stratal oxidation zone wedges out with gray sediments near or inside a flood valley, when the sand alternates with clay or silt, or includes clay pellets and coaly matter. In the cross sections of strataly oxidized zones, such areas are indicated by alternating off-white-yellow well permeable and brown-yellow less permeable rocks [9].

The low Fe contents in strataly oxidized off-white-yellow rocks are responsible for the low level of sorptional uranium accumulation in the lithologic-geochemical setting. A deficit

of U is usually observed here as compared with unaltered gray rocks ($1-2 \times 10^{-4}\%$ and less, against $3-5 \times 10^{-4}\%$), which resolves the question about the source of the ore matter in stratal infiltration in favor of the enclosing sediments.

The white type of stratal oxidation zones is the case where oxygenated water had infiltrated through well-sorted oligomictic quartz sands almost devoid of ferrous minerals - whether clastic or authigenic (Fe_{tot} less than 0.3-0.1%). These are mainly sediments of sea shores (beaches) and shoals (sediments of submerged shallow areas, sandspits, bars, etc.). Another representative of the white type is sand rocks, previously subjected to surface limonitization and to subsequent epigenetic reduction with an intensive iron washout. Oxygenated stratal waters passed through such rocks; stratal oxidation zones did not modify the pigmentation of these rocks to any noticeable degree.

The stratal oxidation processes in these instances are indicated not by the high-permeability white rocks themselves, but by silt-clay rocks which are interstratified with them or occur at their foot or roof and are richer in ferrous iron. Within the stratal oxidation zones, such rocks are inevitably subjected to limonitization and become brown-yellow, indicating oxidative epigenesis to be present also in white sandy lithologic varieties conjugated with them. Uranium metallization can be formed here in the floor and/or roof of the white stratally oxidized zones, at contacts with rocks containing organic matter or other reducers of U(VI). Examples of this kind of metallization, controlled by "horizontal seepage jets," with an anticipating development of stratal oxidation after gleyed sands of the aquifer tops, have been described in [9].

The green-yellow type is represented by zones of stratal limonitization developed after shallow and litoral-marine clay-sand rocks and quartz sands with substantial (up to 3-5%) quantity of authigenic glauconite. The latter gradually becomes brown, and is converted into a mix of hydromicaceous minerals with goethite and hydrogoethite [16].

Observations show that the dull greenish-yellow background of stratally oxidized rocks of this type is due to glauconite-like flaky hydromicas enveloping the clastic matter, rather than the oxidation of glauconite grains themselves. The iron content in hydromica is so low that the brownish-yellow Fe(III) hydroxides form no distinct pseudomorphous segregations, but are, as it were, dissolved in clay green mass.

Stratally oxidized green-yellow zones formed in sands or sandstones of a large thickness, poor in organic content and with a low reducing potential, are not favorable for signs of infiltrational uranium metallization, unless there is superimposed reducing epigenesis.

The pink type of stratally oxidized rocks reflects the development of neomorphous hematite or its aquatic analogs (hydrohematite, turgite, etc.); it is widespread in certain ore formations and areas.

The origins of pink and red pigmentation of rocks in stratal oxidation zones are not quite clear. Kashirtseva [5] determined two varieties of pink-red Fe(III) hydroxides occurring amid stratally oxidized rocks:

- as segments and pseudomorphoses, clots, etc. resulting from oxidation of iron-containing minerals; these hydroxides are connected with yellow-brown Fe(III) hydroxides by gradual transitions; and

- powder dusting on grains without any visible connection with primary iron-containing minerals.

The latter mineral variety occurs azonally relative to the stratal limonitization zone; sometimes superimposed hematite segregations occur even outside the area where these zones wedge out in adjacent gray rocks. The concentrations of total and ferrous iron in such hematized areas are much higher. These are sites of red ferrugination of rock produced by effects of rising reductive solutions which transported iron and deposited it in the oxide from when it was brought into an oxygen environment or in direct vicinity with it [1]. Hematization is often controlled by permeable zones of faults, and there is a close paragenesis with the set of neomorphs of thermal reductive epigenesis: sulfidization, carbonatization, sometimes argillization, silicification, apatitization, bituminization, etc. this issue, however, is beyond the scope of the present paper. Examples of epigenetic hematization (and goethitization) accompanying the near-fault uranium "reduction ores," sometimes superimposed on stratally oxidized rocks, have been given in [1, 2, 10, 15, and others].

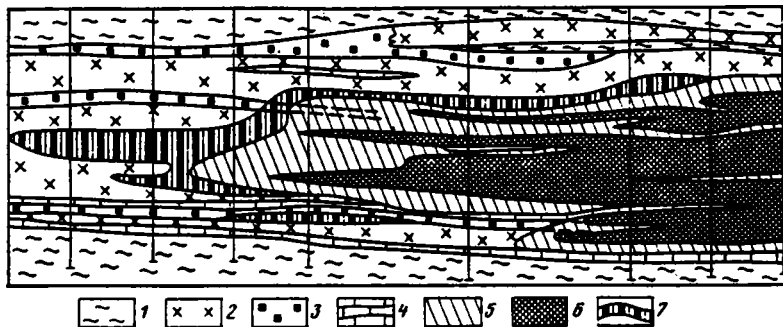


Fig. 3. Position of strataly oxidized pink rocks in the profile of ore-controlling epigenetic zonality in uranium deposit in deltaic Lower Senonian sediments: 1-4) unoxidized rock (1 - clay, 2 - sand with $\text{Fe(II)}_{\text{pyr}}$ less than 0.5%, 3 - same, more than 0.5%, 4 - sandstone layers with carbonate cement); 5-6) strataly oxidized rocks (5 - brown-yellow, 6 - pink); 7) uranium metallization.

Various theories have been proposed concerning the origin of the first pseudomorphous variety of pink-red Fe(III) hydroxides. It was suggested in particular that, unlike brown-yellow hydroxides, the red varieties (hydrohematite) are formed at great (>500 m) depths in conditions of higher temperatures of stratal waters, which oxidize the rock [16]; it was also suggested that these hydroxides mark more ancient (mainly Mesozoic) oxidation zones when the aging of brown-yellow goethite-hydrogoethite segregations converts them into a more stable mineral form, such as hematite or turgite [6].

These two hypotheses, however, are not confirmed by facts. Pink oxidized rocks often succeed yellow rocks in the direction toward the surface outcrops of bed (rather than vice versa), and they are often associated with young Pliocene-Quaternary infiltrational processes; brownish-yellow hydroxides in buried zones of surface limonitization, on the other hand, are preserved since the Mesozoic and in platformal sediments since the Paleozoic, without ever being transformed into red or pink varieties [9].

The totality of data collected by us indicates that if the red ferrugination associated with high-Fe solutions is excluded, the pink oxidized rocks in stratal oxidation zones are usually determined by lithologic and geochemical factors.

In many of the stratal infiltrational uranium deposits in sands and sandstones, the pink oxidized rocks form the rear portions of the stratal oxidation zone, often adjacent to permeable primary red rocks located close to the stratal water supply area. The strips of these epigenetic pink rocks vary in width, depending on the ratio of Fe-Mg chloride and biotite in the original terrigenous rocks on the one hand, and pyrite, siderite, and coaly matter on the other; it is often determined by the position of the belt of facies transitions from initial alluvial sands to sand-clay sediments. When the former mineral components are predominant in the parent rocks, as in polymictic, slightly diagenetically reduced alluvial sands, the epigenetic pink varieties reach the area where stratal oxidation zones wedge out. In flood-valley feldspar-quartz sands with small amounts of clastic biotite and magnesian chlorite, the frontal area of the pink zone is separated from the movement front of the stratal limonitization by 10 to 15 km. In marine well-sorted oligomictic quartz sand, the pink zone is practically absent.

The bipartite structure (the yellow frontal part and the rear pink part) is observed in zones of stratal oxidation in rocks of various age. It has been described in the Jurassic uranium by Stolyarov and Rasulova [11]; deposits in Lower Senonian sand described by Kashirtseva [5]; in the Upper Senonian studied by the present authors; and in ore-bearing Eocene sandstone of the southern Powder River basin (Wyoming, USA) [17].

The ratios of the pink and yellow zones of stratal oxidation in uranium deposits are determined clearly by lithologic-facies features of the enclosing rocks, which are determined by the structure of orogenic deposits. The pink zone usually gives way to a yellow zone, where coal seams appear in the profile, and the former zone is wider the farther these beds appear from the infiltration area.

The structure of the epigenetic zonality of a deposit confined to a cyclically built deltaic Lower Senonian bed is illustrated by Fig. 3.

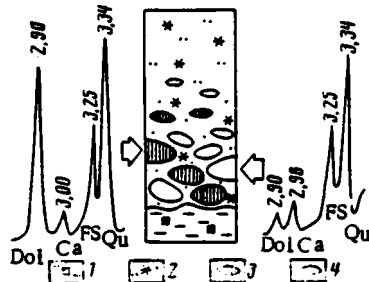


Fig. 4. Correlation between the color of clay rolls in stratal oxidation zone and dolomite content in them (sketch of the rock interval 0.5 m thick and diffractogram fragments): 1) unoxidized gray siltstone with pyrite; 2) oxidized coarse and medium grained sand; 3) pink clay rolls; 4) yellow clay rolls. Letters identify reflections of dolomite (Dol), calcite (Ca), feldspar (FS), and quartz (Qu).

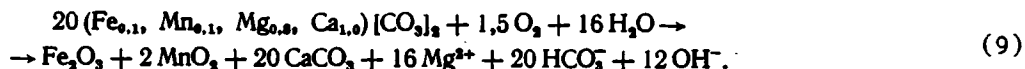
The pink color of the rear part of the stratal oxidation zone is produced by hematite pseudomorphoses after biotite grains (see Fig. 2d) and Fe-Mg-chlorite; hematite forms crustlets and powder segregates next to relicts of these minerals (see Fig. 2e). Pyrite insets in iron-containing silicate grains or near them are also replaced by pink-red iron oxides (rather than brown-yellow, as in frontal part of the stratal oxidation zone) (see Fig. 2f); this is also true of the rare relicts of coaly detritus occurring here.

The pink color is often acquired in stratal oxidation by carbonaceous rocks - dolomite and limestone [12]. In them, pink-red Fe(III) hydroxides develop in pores, cracks, suture-stylolitic seams, mollusk shell valves, oolite concentrers, etc., recording the past occurrence of Fe(II) disulfide, clastic biotite, and chlorite. Where substantial amounts of pyrite are replaced, the carbonate rocks acquire an orange or yellow-brown color.

A correlation between the pink color in stratially oxidized rocks and carbonate matter in them is observed in the permeable Upper Senonian bed, which accumulated on alluvial plane in semiarid climate, and contains numerous intraformational sedimentation interruptions. Diagenetic carbonates (Fe-Mn-dolomite and calcite) are found here as disseminated admixture in flood-valley siltstone and clay, forming cement of basalt conglomerates and coarse-grained sandstones, and building interlayers of hard carbonaceous sandstones - traces of former salt patch soils - inside the members of friable flood valley sands. When stratal oxidation zones are superimposed on these rocks, hematite is formed often, sometimes in association with manganese hydroxides. The pink color of clay pellets in basal horizons of sandstone members is due to the admixture of dolomite (Fig. 4). Pellets without this admixture are yellow.

Carbonate sandstones are colored pink or red by oxidation if MgO contents in the cement is higher than 7% (see Table 1); otherwise they become yellow or yellow-brown. The isomorphous Mn(II) admixture in the parent dolomite in amounts of >0.5% can mask the color of neomorphic Fe(III) hydroxides, producing dark brown or black pigmentation of these areas. Generally, the spotty distribution of pigments in clastic rocks with calcite-dolomite cement is produced by complex combinations of aggregates of iron hydroxides (hematite and goethite groups) and manganese released by Fe-Mn-dolomite oxidation.

Pink and red colors, when magnesium prevails over iron and manganese in the composition of dolomite molecule which, in conformity with the following reactions, results in lixiviation of the medium when the mineral is oxidized:



When the ratios are opposite (Fe or Mn prevails over Mg), the oxidation of these carbonates is accompanied by acidulation of solution (7), and yellow-brown iron hydroxides of the goethite group are released.

TABLE 1. MgO, CaO, MnO, and Fe_{tot} Contents in Differently Colored Sandstones with Carbonate Cement and Massive Structure, %

Color	Number of specimens	MgO	CaO	MnO	Fe _{tot}
Pink, red	4	7,8	15,8	0,35	2,1
Brown	3	3,6	11,4	0,66	1,0
Yellow	6	4,2	12,0	0,30	0,9
Brown	6	0,5	15,8	0,78	2,0

Replacement hematite formation in carbonate layers produces a red pigmentation in the frontal part of the stratal oxidation zone.

When carbonate-rich layers are widespread amid off-white-yellow, or brown-yellow stratally oxidized rocks, yellow-pink varieties are created. The pink-red iron hydroxides color both carbonate layers and adjacent loose sand. Along with pseudomorphoses, globular segregates of cherry red hematite become common.

The yellow-pink type of stratally oxidized rocks is frequent also in carbonate-free sands, where features of an alkaline setting of sedimentary diagenesis appear: neomorphous adularia rims around clastic grains of potassium feldspar and authigenic albite segregates in rock interstices. Pink-red Fe(III) hydroxides are formed around clay pellets on contact with clay layers marking the previous Fe(II) disulfide accumulations; they pigment completely the clay, which include the dolomitic component. Pointlike and larger segregates of pink-red iron hydroxides occurring and yellow rocks produce pseudomorphoses after finely dispersed pyrite contained in shelly montmorillonite segregates.

The combination of data, including the correlation of pink-red Fe(III) hydroxides with oxidation of biotite and Mg-chlorite in the rear parts of stratal oxidation zone and their confinement to carbonate rocks and areas of developed terrigenous rocks with Fe-Mn-dolomite cement and rocks with traits of alkaline sedimentation setting and diagenesis, all indicate that pink (and related yellow-pink) types of stratally oxidized rocks resulted from a heightened alkalinity of the oxidizing medium.

To test this hypothesis and confirm the results of lithologic-geochemical and mineralogic observations, the following experiments were conducted. An acid solution of divalent iron was neutralized with caustic potash, in one case to pH 6-7, and in another case to 9-10. Hydrogen peroxide was rapidly added to the dark-green precipitate, until full oxidation of Fe(II). The process reduced pH, which eventually dropped to 4.0 and 8.5. The sediment dried for 3 h and 85°C after test 1 became brown-yellow and after test 2 became brown-red. After trituration and rinsing, line scratched on the second mineral became cherry red.

Studies of the mineral phases by Mössbauer spectroscopy showed that the product obtained at pH 4.0 was hydrogoethite with heightened water content and Mössbauer parameters $\sigma = 0.55$ mm/sec, $\Delta = 0.7$ mm/sec (Fig. 5a). In the brown-red sediment of experiment 2 (pH 8.5) the isomeric shift ($\delta = 0.5$ mm/sec) and quadrupole splitting ($\Delta = 0.75$ mm/sec) were close (see Fig. 5b) to the parameters of ferrihydrite - the protosubstance of hematite [7].

Chukhrov et al. [3] concluded, on the basis of a large number of tests, that goethite is the only stable Fe(III) oxide in acid and ultraalkaline media. In pH range from ~7.5 to 12.5, this mineral is not formed directly from ferrous iron compounds in the presence of dissolved salicic acid, and gives way to ferrihydrite.

Since epigenetic pink varieties are common in those permeable horizons of sedimentary rocks which are rich in clastic iron-containing minerals and carbonates, and relatively depleted of organics and Fe(II) disulfides, they cannot generally be regarded as an indicator favorable for pay uranium deposits at the wedged-out areas of stratally oxidized zones. The heightened alkalinity of the epigenesis environment marked by pink rocks is conducive to stability of uranyl-carbonate anions in the solution, and interferes with reducing uranium precipitation in wedging-out areas of oxidation zone.

The negative role of these factors can be offset by a contrastive reducing barrier when, for example, a coal seam is present at the foot of the aquifer (uranium-coal type of deposits) or unoxidized rocks of effective epigenetic uranium reducers (bitumines, hydrogen sulfide, or

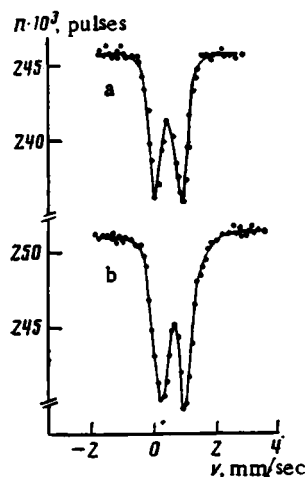


Fig. 5. Mössbauer spectra of the products of experiment 1 (a) and experiment (b): v speed of source, n number of pulses registered.

hydrogen) are present in the zone of unoxidized rock brought previously or parallel to the development of the stratal oxidation process from outside into the ore-containing bed.

In areas of widespread pink oxidized rocks, a reducing barrier can give rise to vanadium as well as uranium metallization. It has been determined [4] that the migration capacity of V in uranium oxygen waters rises with increasing alkalinity of the medium, and starting from pH 8.2-8.3 this element can be transported, along with uranium, in concentrations of $(n \times 10^{-5})$ -($n \times 10^{-4}$) g/liter. The pink zones of stratal oxidation can therefore be interpreted as a prospecting criterion of stratal infiltrational vanadium ore, which is associated also with uranium metallization in roll deposits in limestone [16].

The prospecting value of strataly oxidized zones of the yellow-pink type is determined by their intermediate position between brown-yellow varieties favorable for infiltrational metallization and the less favorable pink varieties.

* * *

The available data thus indicate that the pigmentation of strataly oxidized rocks depends on the facies and paleogeographic characteristics of the parent sediments, which determine the iron contents and the type of its primary mineral form, the position of the segment in the profile of stratal oxidative epigenetic zonality, the alkaline-acid regime of the mineral-forming medium, the presence and type of preceding epigenetic alterations, and the azonal manifestations of the reductive epigenesis, complicating the stratal infiltrational process.

Rocks rich in coaly matter and iron disulfides become brown-yellow during stratal oxidation, as Fe(III) hydroxides develop into goethite-hydrogoethite group. Off-white-yellow color is observed in zones of stratal limonitization, developing in iron-poor sands with low contents of dark components; white varieties occur in well-sorted sands, and develop after oligomictic sand and rocks previously subjected to surface oxidation and gleying; green-yellow pigmentation is produced by stratal oxidation of glauconite-containing sand and clayey sandstone.

Pink color of strataly oxidized rocks is due to the presence of neomorphous Fe(III) oxides of hematite group, and usually indicates a heightened alkalinity of the environment. It can be a result of general oxidation sequence of iron-containing minerals (an alkaline wave at the rear of the stratal oxidation zone, where biotite Fe-Mg-chloride, and Fe-dolomite are decomposed) or local geochemistry of the lithologic setting (oxidation of rock portions rich in alkaline and alkaline-earth elements). In conformity with these features, the oxidized rocks acquire sometimes spotty or striated pigmentation where coaly remains, pyrite, siderite, and Fe-chlorite are replaced by brown-yellow iron hydroxides, while biotite, Fe-Mg-chlorite, and Fe-Mn-dolomite are replaced by pink-red varieties. When ferruginous minerals rich in alkalis and alkaline earths are an important component of the parent rocks, resulting in heightened alkalinity of mineralization environment, even pyrite and organic remains can be replaced by pink-red hydroxides.

For other conditions being equal, brown-yellow varieties and off-yellow and white forms interstratified with brown-yellow ore replaced by them are of most interest in searching for uranium metallization in areas where the stratally oxidized zones wedge out. The stratally oxidized zones fully made up of off-white, yellow-white, and green-yellow or pink types can be associated with pay deposits of uranium only when azonal signs of reducing epigenesis are present in the beds. Pink zones of stratal oxidation can be associated with an epigenetic vanadium mineralization.

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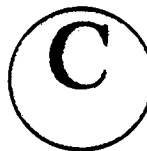
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